

## HEATING OF COAL WITH LIGHT PULSES

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Introduction

The carbonization of coal is normally carried out under conditions of relatively slow heating, the process taking many hours. During the past decade, interest has arisen in faster heating rates. Thus, the use of fluidized beds<sup>1</sup>, circulating heated pebbles<sup>2</sup>, and hot-gas<sup>3</sup> carbonization treatment has reduced the heating periods into the time range of seconds or less. Investigators have reported in detail carbonizations in time ranges as low as 60 milliseconds<sup>3</sup>. Nelson reported the use of flash heating on coal samples but did not detail his findings<sup>4</sup>. His technique resulted in one to three milliseconds exposure. The present work was undertaken to obtain further information on the effect of flash-heating on coal using even shorter exposures.

Experimental

The flash unit consisted of a flashtube holder, four 100 $\mu$ F capacitors, and a 4000V power supply. A GE FT524-Xenon-filled quartz helix flashtube was used. The flash unit was incorporated into a gas-handling system as shown in Figure 1.

The duration of flash is a function of the electrical circuit, particularly the capacitance and the resistance of the flashtube. By definition, the flash duration is considered to be the time from the initial 1/3-peak power to the final 1/3-peak. With a given tube, the length of the flash varies with the capacitance. The flash duration was determined from data supplied by the manufacturer<sup>5</sup>, Table I.

TABLE I  
Flash Characteristics

Capacity	Time above 1/3 power, $\mu$ sec.		Input, joule	Output, j/sq. cm. <sup>4/</sup>
	Max.	Min.		
100 $\mu$ F	230	195	800	3.7
200	-	305	1600	7.5
300	-	415	2400	11.2
400	800	520	3200	15

\*The internal surface of the helix is 62 sq. cm.

The input energy dissipated in the flash was computed from the formula  $E = 1/2 CV^2$ , where E is the energy in joules, C is capacitance in microfarads, and V is voltage in kilovolts. Thus, the FT524 tube emits 15 optical joules/sq. cm. for an energy input of 3200 joules. But, as seen above, the light energy output is considerably less than the input energy. Approximately 30 percent of the input energy was radiated into the test cylinder.

The experimental system used is shown in Figure 1. Usually 10 mg. of pulverized coal (less than 10 microns in size) were transferred into the quartz reactor and suspended on the walls by rotating the reactor. The reactor was then carefully placed into the helix of the flashtube, connected to the manifold, and evacuated. After flashing at the desired energy level, the pressure rise was measured and a gas sample was taken. The residual solids were sampled or weighed when necessary.

As the characteristics of both the lamp and the quartz reactor tended to change with time, test series designed to achieve specific goals were run closely together.

### Results

A series of coals having increasing volatile matter content were studied. Their compositions and proximate analysis are shown in Table II.

TABLE II  
Composition of Coals Used

Coal	<u>Elkol<sup>1</sup></u>	<u>Federal No. 1<sup>2</sup></u>	<u>Kopperston No. 2<sup>2</sup></u>	<u>Colver<sup>2</sup></u>
<u>Proximate Analysis,</u>				
%, dry basis				
Volatile Matter	40.7	37.7	31.6	25.3
Fixed Carbon	54.6	56.8	63.9	68.5
Ash (dry)	4.7	5.5	4.5	6.2
<u>Ultimate Analysis,</u>				
%, dry basis				
Carbon	70.6	78.4	85.1	80.6
Hydrogen	5.4	4.9	6.2	5.3
Sulfur	1.0	1.9	0.7	0.8
Nitrogen	1.2	1.5	1.5	1.5
Oxygen	17.1	7.8	2.0	5.6
Ash	4.7	5.5	4.5	6.2

<sup>1</sup>Kemmerer Coal Co., Frontier, Wyoming

<sup>2</sup>Eastern Gas and Fuel Associates, Pittsburgh, Pa.

The composition of the evolved gases from the last three coals is shown in Figure 2 through 4. As the energy of the flash is increased, the gas composition changes. Hydrogen increases, the volume percentage of  $C_2H_2$  remains nearly constant, while the more saturated hydrocarbons decrease.  $CO_2$  decreases, while  $CO$  increases.

The gas-composition trends are consistent with increased cracking of the evolved gases with the higher temperatures associated with the increased energy. Thus, the more saturated ethane and ethylene are replaced by acetylene. Also, methane may crack to acetylene. However, the acetylene may decompose to carbon and hydrogen.

It is of interest to relate the product concentration to the volatile matter of the coal. The younger coals show less hydrogen and methane in the product gas. However, increasing the energy input increases the concentration of both of these gases, Figure 5.

Tests were also run to determine the effect of various atmospheres on the product distribution. As stated previously, most of the experiments were run in vacuum. In a departure from this usual practice, nitrogen was added to serve as an absorber for the high energy believed existent in the products. It is seen in Table III that 10 mm. of  $N_2$  had no significant effect, when compared with the vacuum runs.

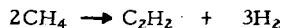
TABLE III

Effect of Increased Pressure

200- x 325-mesh Elkol particles, 3200 joules input

Gas Composition, mol %	10 mm $N_2$	Control (vacuum 0.1 mm)
$H_2$	44.5	42.4
$CH_4$	0.9	0.7
$C_2H_2$	20	20.7
CO	24.5	25

The effect of hydrogen in repressing the decomposition reactions was investigated next. Two pressure levels were investigated. It is seen in Table IV that increasing the  $H_2$  pressure decreases the  $C_2H_2$  while increasing the  $CH_4$ . This is consistent with inhibiting the reaction.



Some saturation of the  $C_2H_2$  could also have occurred. Increasing the pressure increased the effect. Two sets of control runs are quoted because the tests were run at different times and the physical conditions of the reactor, light, etc. had changed.

TABLE IV

Effect of Hydrogen

Elkol 5-10 $\mu$ , 3200 joules energy input

Gas Composition	Mole % (on $H_2$ -free basis)			
	Higher pressure comparison		Lower pressure comparison	
	160 mm $H_2$	control (0.1 mm vacuum)	10 mm $H_2$	control (0.1 mm vacuum)
$CH_4$	4.8	0.8	0.4	0.4
$C_2H_2$	9.5	25.0	25	37.8
CO	85	65.5	71	49

The effect of steam on the reaction was studied by adding a drop of water to the coal. As shown in Table V results are similar to those obtained with  $H_2$ .

TABLE V

Effect of Water

Elkol, 3200 joules energy input

Gas Composition. mol %	With $H_2O$	Without $H_2O$
$H_2$	48	59
$CH_4$	2.6	1.0
$C_2H_2$	8.2	14.7
CO	30.1	21.4
$C_2$ 's	4.9	2.7

In the above results, all changes were attributed to variation of the energy input. However, the exposure time varied concurrently. With the available set-up, it was not practical to vary the electrical circuitry. Mechanical screening of the coal proved most practical as a means of varying the energy at constant exposure time. The technique consisted of using a double quartz reactor and interposing three layers of 18- x 14-mesh metal screen between to cut down the adsorbed energy without affecting the time, Table VI. It is seen that the screen, by reducing the impinging energy, reduces cracking reactions.

TABLE VI

Effect of Energy Variation on Yield

Double Quartz Walls

Elkol coal, average particle size 5-10 $\mu$

	<u>With Screen</u>	<u>Without Screen</u>	<u>Without Screen</u>
Electrical Energy input	3200j	3200j	800j
Gas Composition. mol %			
$H_2$	16	59	44
$CH_4$	5.5	1.0	3.0
$C_2H_2$	4.2	14.7	12.0
CO	53	21.5	18
$CO_2$	7.7	0.4	2.3
$C_2$ 's	8.9	2.7	6.6
$C_3$ 's	2.0	-	1
$C_4H_2$	0.2	0.7	0.8

Mass balances around the reactor show recoveries of 74 to 110 percent. The weight of gas was determined from the pressure rise. The solid residue was washed into a Celite filter-aid bed for weighing. In none of the tests was there any evidence of tar formation. As seen in Table VII, the amount of gas produced varied randomly, reflecting poor reproducibility in exposing all of the coal to the flash. Some of the coal invariably fell to the bottom of the reactor during handling. Also, some coal obviously was blown from the reactor wall during the volatile-matter release.

TABLE VII

Mass Balances

All runs at 3200 joules energy input

Coal	Wt. Charged, mg.	Recovery, mg.		% Recovered
		Wt. Solid	Wt. Gas	
Elkol	10.6	5.4	3.2	81
Elkol (N <sub>2</sub> run)	10.2	5.5	6.2	115
Elkol (H <sub>2</sub> run)	10.4	6.9	4.0	105
Elkol (H <sub>2</sub> run)	11.3	8.6	3.8	108
Johnstown	9.7	8.5	1.7	105
Johnstown	10.7	6.7	1.8	80
Johnstown	10.1	8.5	2.5	110
Powhattan	10.1	6.3	2.9	92
Powhattan	10.0	7.6	2.8	104
Illinois No. 6	10.4	8.8	1.4	98
West Virginia	10.3	4.8	2.8	74
West Virginia	9.7	6.0	2.6	89

Since the distribution of solids and gas did not give a realistic estimate of the percentage of coal volatilized, various other techniques for obtaining this parameter were investigated, but none were successful.

Microscopic examination of the residues showed the presence of carbon-black particles. The presence of these particles could be interpreted as being the residue of almost completely vaporized coal particles or the final product of a hydrocarbon-cracking sequence. A variety of tests were therefore devised to clarify this point.

1) In order to preserve as much of the hydrocarbons as possible, an even faster quench was attempted. A special reactor vessel with a central cooling thimble was constructed by suspending a small 4-inch test tube within

a larger one. The thimble was filled with either a dry ice-acetone mixture or liquid nitrogen. At first, the cold thimble was placed above the top of the flash tube. Black sooty material was found all over the condenser indicating that gas-phase decomposition could have occurred. The thimble was lowered until it was finally completely within the flash zone. When liquid nitrogen was used, the thermal shock shattered the glass apparatus. However, the sooty appearance of the condensed particles persisted.

2) Attempts were made to distinguish microscopically between unreacted coal, char and acetylene black. The fineness of the starting material made direct decision among the possibilities impossible. Attempts to produce very uniformly sized coal were essentially unsuccessful. It was finally decided to attempt direct comparison by photographing specific areas of slides before and after flashing. The results are shown in Figure 6. The A designation indicates that the picture was taken before flashing, the B, after flashing. The grid was superimposed on the slides during printing and serves to locate points of interest. It can be seen that large clumps of coal were blown off the slide by the flash. For example, compare Figure 6A - B areas 7D, 2F. Some glass was blistered as in Figure 6B, areas 8D, 9F. Important observations can be made in Figure 6A - B, areas 8D, 8E - F. Here particles can be identified before and after exposure (note in particular the particle shaped like the state of New Jersey in the upper center of 8D). The particles are essentially similar in shape before and after the flash, thus indicating that complete decomposition of the coal has not occurred. Obviously these coals were not screened from the flash, as any particle which could be seen by the camera should also have been exposed to the flash. The conclusion therefore must be that only partial vaporization or decomposition of the coal particles occurred. However, the exact magnitude cannot be determined since the coal particles expand during the coking process.

### Conclusions

Flash heating is a practical technique to produce short periods of high temperature in coal particles. The percentage of coal volatilized could not be determined, but microscopic examination suggests that total vaporization did not take place. No liquids were recovered, but the gases, whether produced directly or indirectly by cracking of precursor tars, contained many valuable constituents.

### Acknowledgment

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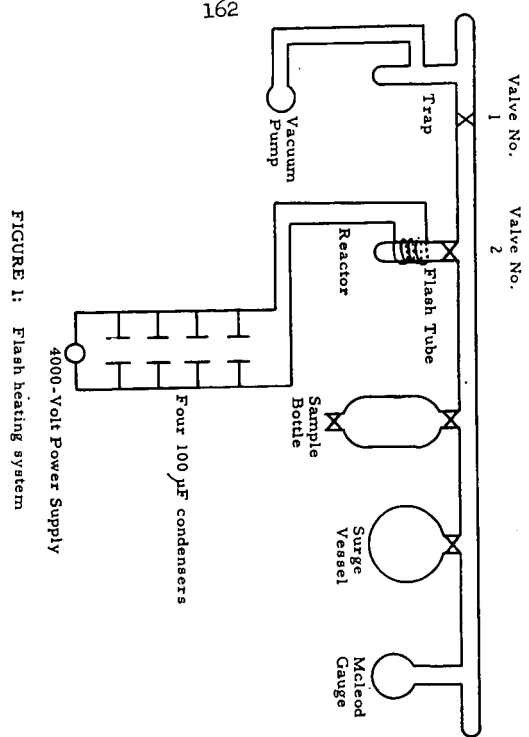


FIGURE 1: Flash heating system

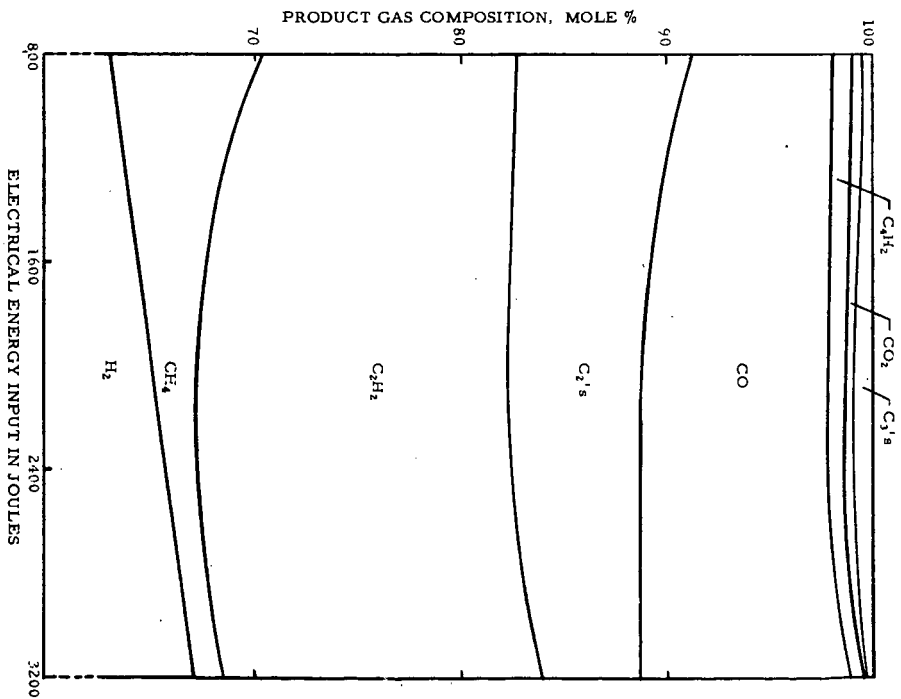


FIGURE 2: Gas composition from flash heating of Federal No. 1 coal (-400 mesh then pulverized), Quartz reactor

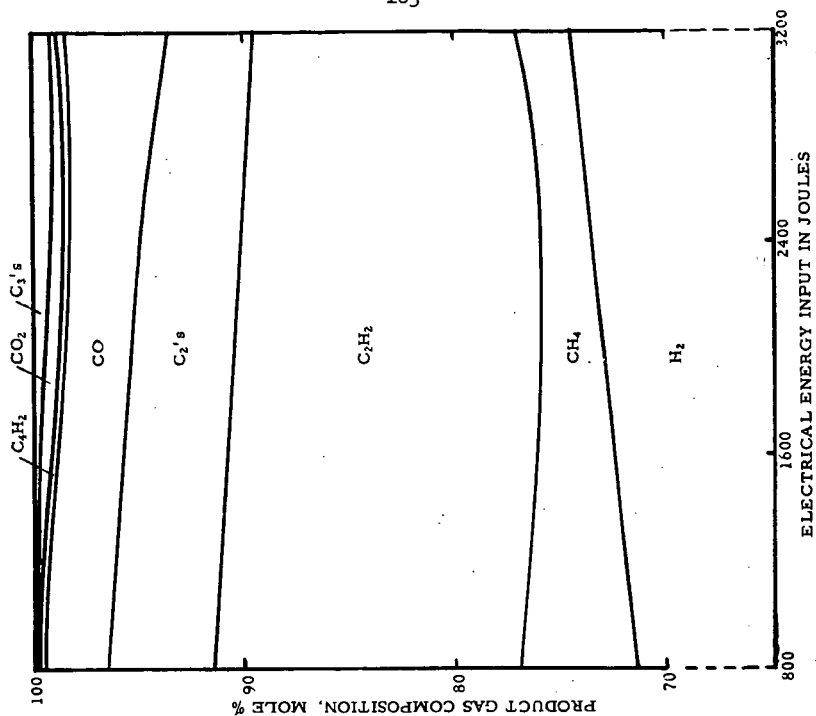


FIGURE 4: Gas composition from flash heating of Colver coal (-400 mesh then pulverized), Quartz reactor

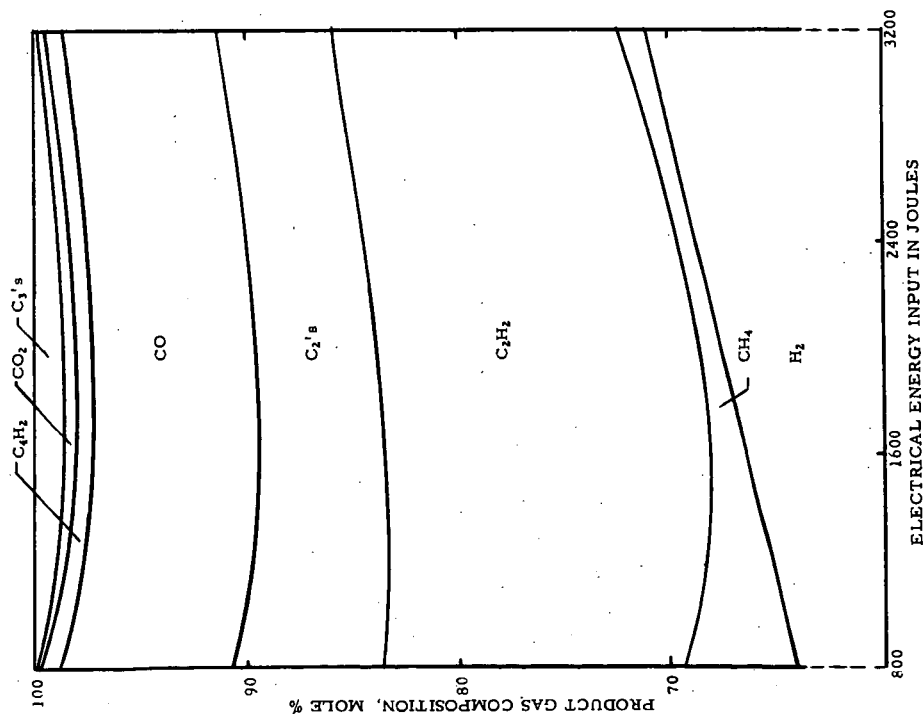


FIGURE 3: Gas composition from flash heating of Kopperston coal (-400 mesh then pulverized), Quartz reactor

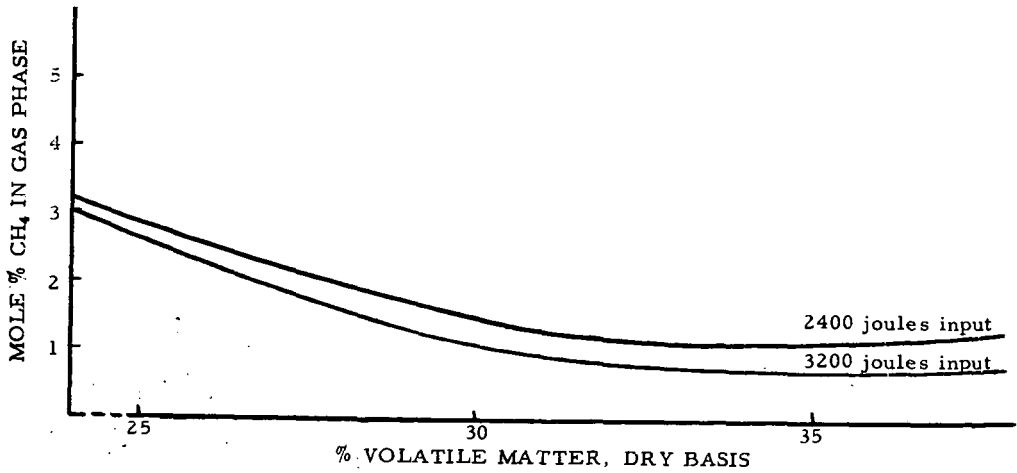
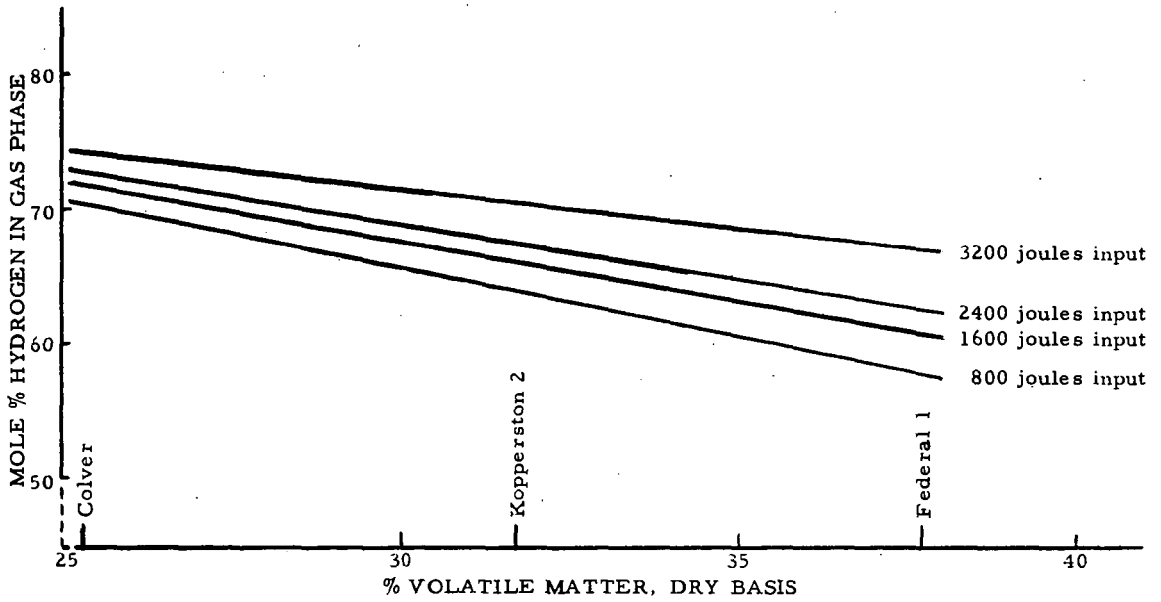


FIGURE 5: Relationship of H<sub>2</sub> and CH<sub>4</sub> concentrations to volatile matter of coals



FIGURE 6A: Before flash Each scale division = 2 microns  
Energy of flash 3200 joules.  
Elkol, powdered, then twice elutriated to separate out  
the fines; average particle size about 5 microns.



FIGURE 6B:      After flash      Each scale division = 2 microns  
Energy of flash 3200 joules.  
Elkol, powdered, then twice elutriated to separate out  
the fines; average particle size about 5 microns.

## Extensive Reduction of Coal by a New Electrochemical Method

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In recent years electrolytic methods have been employed in the reduction and structural elucidation of coal (1, 2). The usefulness of these methods is limited by the fact that the benzene ring (that is, the isolated benzene ring as in benzene or tetralin) which may represent a large portion of the coal structure, has not previously been reduced electrolytically. Work in this laboratory has shown that reduction of benzene can be achieved by electrolysis in ethylenediamine saturated with lithium chloride (3). The same method has now been successfully applied to the reduction of a high rank coal and has resulted in the addition of 36 hydrogens per 100 carbon atoms. The best electrochemical reduction achieved (2) prior to this amounted to the addition of 14 hydrogens.

### EXPERIMENTAL

Six grams of the coal (Pocahontas vitrain ground to pass 325 mesh) suspended in 100 milliliters of ethylenediamine containing 1.4 grams of lithium chloride was electrolyzed at 33° between carbon electrodes at 0.5 amperes and 115 volts. Apparatus and technique of electrolysis (3) and recovery of the reduced coal (4) were the same as described previously. Current efficiency at the beginning of the electrolysis was 46 percent and dropped to 10 percent after 16 hours. The electrolysis was continued for an additional 15 hours during which time the current efficiency remained practically constant. The reduced coal was recovered from the solution, analyzed and subjected to a second electrolytic reduction. The current efficiency at the beginning of the second electrolytic reduction was 20 percent and dropped to 8 percent after 16 hours. The electrolysis was continued for 15 hours during which time the current efficiency remained at 8 percent. Recovery of the reduced coal was 95 percent. The reduced coal was tan-gray in color and 73 percent soluble in pyridine; the solubility of the unreduced coal was only 3 percent. The analyses of the original and reduced samples are shown in Table 1. The ratio of total hydrogen taken up by the coal to lithium chloride used was about 2:1.

### DISCUSSION

Perhaps the most interesting result is the fact that the solubility of the electrolytically reduced coal in pyridine at room temperature (73 percent) is higher than that of the same coal reduced chemically (4) with excess lithium in ethylenediamine at 90-100°. In the latter case, 45 hydrogens were added but the solubility was only 63 percent. It is conceivable that chemical reduction at elevated temperature, in contrast to electrolytic reduction at room temperature, is accompanied by polymerization resulting in a decrease in solubility.

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TABLE 1. - Electrochemical reduction of Pocahontas vitrain

Substance	C	H	N	S	Ash	H atoms added <sup>a</sup> per 100 C atoms in starting material
Original vitrain	87.94	4.53	1.12	1.01	3.10	
	88.09	4.58	1.15	0.97	2.98	
First reduction	81.82	6.29	2.93	1.12	3.97	21.1
	81.77	6.15	3.29	1.21	3.76	
Second reduction	80.81	7.21	3.82	0.31	3.85	36.1
	80.73	7.19	3.80	0.51	3.21	

<sup>a</sup> Method of calculation as described in reference 4.

## Destruction of the Caking Quality of Bituminous Coal in a Fixed Bed

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### INTRODUCTION

Production of a high-Btu pipeline gas from coal appears to have great potential for consuming coal in large quantities. Fixed-bed pressure gasification with steam and oxygen is highly attractive for the production of high-Btu gas because a gas with a high methane content is made with comparatively low oxygen requirements. However, strongly caking coals cannot be gasified efficiently in a fixed bed because they agglomerate and fuse when heated through their plastic range. This would render a fixed-bed gasifier inoperable. Most coals found in the East and Midwest, where the largest markets for pipeline gas exist, are highly caking.

Numerous commercial processes <sup>1, 2, 3/</sup> have produced a noncaking fuel from bituminous coal for many years; however, each was developed for a specific purpose other than for fixed-bed gasification, and was not particularly suited as a preliminary to gasification. Consequently an experimental pilot plant program was initiated by the Bureau of Mines to develop a process for pretreating a caking bituminous coal specifically for fixed-bed gasification. Based upon the general knowledge that thermal or oxidative treatment or a combination of the two destroys the caking property of coal, a process was envisioned which would utilize the above. An integrated pretreatment and gasification scheme appeared advantageous whereby all or part of the feed gases to be fed to the gasifier, or the hot, raw product gas could be used in the pretreatment, and the volatile matter evolved during pretreatment could be returned as fuel to the gasifier.

Use of thermal pretreatment in an oxidizing atmosphere for treating a highly caking coal of granular or small lump size in a fixed bed presented difficult problems. To make particles of this size nonagglomerating, the treatment would have to be drastic enough not only to affect the surface, but also the interior. Furthermore, because the coal expands on heating, compaction in a fixed bed would be difficult to avoid.

Therefore, the purpose of this investigation was first to determine whether the caking properties could be destroyed sufficiently in a fixed bed, and secondly to determine the conditions requiring the minimum time and



effecting the minimum loss of coal. The criterion of successful pretreatment would be that the pretreatment could be completed without agglomeration, and that after pretreatment the coal would not agglomerate in a hydrogen-rich atmosphere at conditions of temperature and pressure similar to those in a fixed-bed gasifier.

## EXPERIMENTAL EQUIPMENT AND PROCEDURE

### Description of Apparatus

The schematic flow diagram of the pilot plant for coal pretreatment given in figure 1 consists primarily of a gas heater and a vessel in which the coal can be heated and exposed to various atmospheres at controlled rates. The vessel is a 4-foot long, 3-1/2-inch diameter schedule 80 pipe made from 304 stainless steel. It is shown in figure 2. A ring joint blind flange served as a charge port and closure at the top of the vessel. The bed of coal was supported by a perforated stainless steel plate located 2 inches above the bottom of the vessel as shown in figure 3. During all pretreatment tests the coal was always heated externally by electric heaters and internally by the pretreating gas. The gas was heated by passing it through a coiled tube located in an electric furnace.

Gases flow normally up through the coal and out of the top of the vessel; however, several tests were performed with gases flowing down through the bed. Either nitrogen, carbon dioxide, or steam, or a mixture of these gases was satisfactory for pretreatment. In the remainder of this report the term "inert gas" is used to represent any of these gases. In some steps oxygen was also required, and this is specified in the procedure.

Temperatures of the bed were measured by thermocouples inserted in thermowells located in the center and at the periphery of the pretreater vessel. Thermocouples were adjustable and normally measured the temperature of the top, center, and bottom of the bed. The thermowells entered the bottom of the vessel and extended within one foot of the top flange. A differential pressure instrument measured and recorded the pressure drop across the fixed bed of coal. Temperature, pressure, and flow control are provided for at the panel shown in figure 4.

### Procedure

The following steps of pretreatment destroyed the caking property of a bituminous coal in a fixed bed,

1. Coal, from 1/8- to 1-1/2-inch size, was heated from ambient temperature to its initial softening temperature as rapidly as possible with an inert gas. This temperature varies with the type or rank of coal, and usually is higher than the softening temperature indicated by the Giesler Plastometer Test (ASTM D-1612-SOT).

2. Coal was held at softening temperature for about 1 to 3 hours with an inert gas containing about one volume percent of oxygen. About 17 percent of the volatile matter was removed during this step.

3. Coal was heated through its plastic range in about 1/2 to 1 hour with a superficial linear gas velocity that varied from 0.6 to 12 feet per second, depending upon the pressure and the oxygen content of the inert gas. An additional 33 percent of the volatile matter was removed, leaving about 50 percent of the original volatiles in the pretreated char.

As an alternate to steps 2 and 3, the coal could be effectively pretreated by gradually heating through its plastic range in about 3 hours. A pretreatment was considered successful after the coal was heated through its plastic range without agglomeration in a fixed bed. The char so produced flowed as freely as the original coal.

#### Testing of Chars and Coals

An arbitrary test was devised in which chars produced by pretreatment were exposed in a fixed bed to hydrogen or hydrogen-rich atmospheres for 1 hour at 400 psig and 600° C. The hydrogen-rich atmospheres contained nitrogen, steam, carbon dioxide, and carbon monoxide. These tests simulated gas compositions and conditions which would be found in a coal gasifier. Chars produced from coals heated through their plastic range without caking in a fixed bed never caked during these tests, indicating a strong probability that a char so produced would not cake in an actual gasifier. Coals not heated through their plastic range invariably caked during the hydrogen test.

Free swelling index (FSI) ASTM Test D-720-57 values of about 1.5 or less, which is usually indicative of a noncaking coal, were recorded for all chars made from coals pretreated through their plastic range. Chars with FSI values were used as a guide in estimating the caking property of chars produced during pretreatment. The ultimate and proximate analyses of coals tested and chars produced were performed according to ASTM procedure D-271-48.

#### Material

High-volatile A bituminous (hvab) coal from the Pittsburgh seam, one of the most strongly caking coals, was used in most of the pretreatment tests. Hvab coals from Sewickley, Upper Freeport, and Taggart seams, in addition to a high-volatile (hvbb) coal from the Illinois No. 6 seam and a low-volatile bituminous (lvb) coal from the Pocahontas No. 4 seam, were also tested and successfully pretreated. Analyses of coals tested are shown in table 1.

#### RESULTS

An example describing a successful pretreatment is as follows: A Pittsburgh seam coal was heated with steam, at atmospheric pressure, containing about 1 percent oxygen and flowing at a superficial velocity of 3 feet per second, to its initial softening temperature of 360°-370° C and maintained at that temperature for 3 hours. It was then heated through its plastic range of 370° to 430° C in about 1/2 hour with the same gas at the same velocity and pressure. The treatment was terminated with nitrogen

TABLE 1.- Source, analysis, free swelling index, rank, and heating value of coals tested

County, bed, mine	Proximate, percent			Ultimate, percent					Heating value, Btu (dry basis)	Free swelling index	1/ Rank
	Moisture matter	Volatiles fixed carbon	Ash	H	C	N	O	S			
<u>Illinois</u>											
Franklin Illinois #6 Old Ben #21	8.0	35.4	50.0	6.6	5.5	70.6	1.7	14.7	0.9	13,550	4.5 hvbb
<u>Pennsylvania</u>											
Allegheny Pittsburgh Federal Bureau Mines, Ex- perimental	2.5	35.6	54.3	7.6	5.3	75.8	1.5	8.2	1.6	13,960	8.5 hvab
Butler Upper Freeport Coal Hollow #2	1.7	35.3	55.9	7.1	5.3	76.9	1.5	7.9	1.3	14,020	8.0 hvab
<u>Virginia</u>											
Wise Taggart Dixiana	1.4	33.8	62.3	2.5	5.3	82.8	1.5	7.2	0.7	14,980	8.5 hvab
<u>West Virginia</u>											
McDowell Pocahontas #4 Bartley #1	2.7	14.8	76.5	6.0	4.4	83.3	1.3	4.5	0.5	14,660	6.5 lvb
Monongalia Sevickley Christopher #5	1.1	36.7	50.9	11.3	5.1	73.3	1.5	6.2	2.6	13,400	9.0 hvab

1/ American Society of Testing Materials, Standard Specifications for Classification of Coals by Rank:  
ASTM Designation D-388-38 ASA #20.1-1938.

cooling the char to less than 100° C in about 1/2 hour. An inert gas containing nitrogen and carbon dioxide was also used to cool the pretreated coal during other tests. A free flowing char was produced with a FSI indicative of noncaking coal. The treated coal expanded about 50 percent above its original volume.

Heating coal with this same gas through its plastic range in 3 hours also produced free flowing char. Replacing steam with nitrogen or nitrogen plus carbon dioxide or a combination of all three gases plus a small amount of oxygen destroyed the caking property of coal in a fixed bed as effectively as the steam-oxygen mixture.

Heating coal, as described previously, with a gas containing 0.2 percent oxygen plus 11 to 40 percent hydrogen and the remainder nitrogen, carbon dioxide, and steam produced a solid mass of char with no evidence of pretreatment. This was an attempt to pretreat coal with a gas similar in composition to a gas produced in a coal gasifier.

The pretreatment technique developed in a 6-inch bed depth at atmospheric pressure with gas flowing up through the bed also proved effective in an 18-inch bed depth with the gas flowing up or down. The bed expanded less during the tests with the gas flowing down; however, the char produced was free flowing and showed no evidence of fusion.

Pretreatment at pressures of 50, 150, and 300 psig in a 6-inch bed depth also was effective. Char produced at elevated pressures normally exhibited less expansion than that made at atmospheric pressure.

The caking quality of hvab coal from the Sewickley, Upper Freeport, and Taggart seams was as effectively destroyed as the Pittsburgh seam coal. Of the four hvab coals tested, Pittsburgh and Upper Freeport seams required about 180 minutes of treatment at 360° to 430° C as compared to about 190 and 200 minutes, respectively, for the Taggart and Sewickley seams. The volatile matter of all hvab coals decreased during pretreatment from about 36 to 20 percent. Pretreatment of the hvbb coal from the Illinois No. 6 seam with a high inherent moisture content of about 8 percent was relatively easy, requiring only 80 minutes at 360° to 430° C. A low-volatile bituminous (lvb) coal from the Pocahontas No. 4 seam containing about 15 percent volatile matter was successfully pretreated at its plastic range of 470° to 510° C in about 2 hours with steam plus oxygen. The volatile matter content decreased from 15 to 9 percent during pretreatment. Analyses of chars produced from these coals during typical pretreatment are shown in table 2.

Expansion of coal during pretreatment was related to gas velocity and pressure. Low velocities or high pressures produced less expansion. Coals with high volatile matter content appeared to expand more. Pretreatment appeared more difficult for hvab coals with a low oxygen content.

Pretreatment at gas velocities approaching fluidization velocities of about 13 feet per second appeared easier and required about 2 hours at 360° to 430° C as compared to 3 hours at a velocity of 3 feet per second. At high gas velocities, the oxygen concentrations in the pretreating gas were varied

TABLE 2.- Analysis, free swelling index and heating value of chars produced during pretreatment with steam containing 1 to 3 volume percent oxygen at atmospheric pressure

Char prepared from bed	Proximate, percent				Ultimate, percent				
	Moisture	Volatile matter	Fixed carbon	Ash	H	C	N	O	S
Illinois #6	0.7	23.3	66.4	9.6	4.3	75.2	1.9	8.1	0.9
Pittsburgh	.3	20.9	71.9	6.9	4.1	78.9	1.7	7.4	1.0
Upper Freeport	.5	22.6	66.8	10.1	4.2	76.0	1.7	6.6	1.4
Taggart	.2	23.1	73.2	3.5	4.4	83.6	1.6	6.3	0.6
Pocahontas #4	.8	8.9	81.8	8.5	3.1	82.8	1.3	3.8	.5
Sewickley	.6	22.1	62.9	14.4	4.0	71.8	1.6	6.4	1.8

Char prepared from bed	Heating value, Btu (dry basis)	Free swelling index	Maximum pretreatment, temp., °C
Illinois #6	13,220	NC <sup>1/</sup>	430
Pittsburgh	13,580	NC	430
Upper Freeport	13,300	1.0	430
Taggart	14,560	1.5	430
Pocahontas #4	13,830	NC	510
Sewickley	12,460	1.5	430

<sup>1/</sup> NC = Noncaking.

from 0.5 to 4.0 percent with good results, whereas at gas velocities of 3.0 feet per second, oxygen content was limited to a range of about 1.0 to 3.0 percent. Low oxygen concentration in the gas is desirable because it allows for close control of the temperature. In tests with oxygen concentrations above 5 percent, temperature control was difficult because of excessive localized combustion.

Figure 5 shows a typical raw coal used plus a char from a successful pretreatment, and the same char after exposing it to a hydrogen flow at 400 psig and 600° C for 1 hour in a fixed bed. There was no evidence of fusion and the char flowed as freely as raw coal. All chars produced during successful pretreatment and subjected to this test did not fuse, or show any evidence of fusion.

Char produced in the manner described from a Pittsburgh seam coal was successfully gasified in a bench-scale, fixed-bed reactor with steam at 800° C and atmospheric pressure at the Bureau of Mines Coal Research Center in Morgantown, W. Va. There was no evidence of caking during gasification, and the results indicate that the char is quite reactive. Even mildly caking coals agglomerated in similar tests.

Tests performed by the Direct Coal-Conversion group at the Bureau of Mines Coal Research Center in Bruceton, Pa., in bench-scale equipment show that the same char as above could be hydrogenated at 3,000 psig and 750° C in free-falling bed without agglomerating. The char was crushed to a 30 x 50 U.S. Tyler mesh size for the hydrogenation tests.

#### DISCUSSION OF RESULTS

Results from tests performed at conditions other than those outlined in the procedure for successful pretreatment indicate the need for close adherence to the procedure. Several of these tests are described: Coal particles heated directly through their plastic range with inert gas in a fixed bed fused into a solid mass as shown in figure 6. Coal particles heated slowly through their plastic range with a gas containing 11 to 40 percent hydrogen plus 0.2 percent oxygen and the remainder nitrogen, carbon dioxide, and steam, also fused into a solid mass similar to the one shown in figure 6. This test was an attempt to pretreat coal with a gas which was similar in composition to a gas produced in a coal gasifier.

Coal heated at its softening temperature of 360° to 370° C with inert gas plus oxygen for 3 to 8 hours, and not heated through the plastic range, also fused upon subsequent exposure to hydrogen at 400 psig and 600° C; however, as shown in figure 7, there was some evidence of pretreatment since discrete coal-char particles were discernible in the fused mass.

Investigators<sup>4, 5</sup> have shown that oxygen was necessary for the reduction or destruction of the caking quality of coal in fluidized or moving fixed beds; however, evidence of complete and relatively rapid destruction of the caking property of coal in a stationary fixed bed was lacking. Consequently, the techniques as previously described were developed using small amounts of oxygen and a controlled heating cycle to destroy the caking quality of coal

in a fixed bed. The role that oxygen plays in helping to destroy the caking property of coal in a fixed bed is not precisely known. However, it is theorized that the "sticky" matter which is normally formed when coal is heated through its softening and plastic range is oxidized to a "nonsticky" material.

The apparent differences in pretreatment time for the coal tested can also be attributed to oxidation. According to Radmacher<sup>6</sup> the rate of oxidation; that is, "the rate of decaking", is generally dependent on the oxygen content of the coal. On the other hand, Schmidt<sup>7</sup> reports that a lvb coal with a low oxygen content was also relatively sensitive to oxidation. This appears to confirm our findings since the hvbb coal from the Illinois No. 6 seam, having the highest oxygen content of about 9.0 percent, required a minimum pretreatment time of about 80 minutes. A pretreatment time of about 120 minutes was required for the lvb coal from the Pocahontas No. 4 seam, which contained about 2.4 percent oxygen.

Pretreatment time for the hvab coals generally was related to the oxygen content. The Pittsburgh and Upper Freeport coals, having an oxygen content of about 7.0 percent, required about 180 minutes of pretreatment, followed by about 190 minutes for the Taggart seam and 200 minutes for the Sewickley seam. Both Taggart and Sewickley seams had a slightly lower oxygen content of about 6.0 percent. The slight difference in pretreatment time for these two coals could be attributed to the differences in volatile matter content, since the Taggart seam had a volatile matter content of about 35 percent compared to 42 percent for the Sewickley seam.

Chars produced from hvab and hvbb coals containing a volatile matter content of 20 percent or less always had a FSI indicative of a noncaking coal. On the other hand, even after it was heated at temperatures that destroyed the caking quality of hvab coals, a lvb coal with a volatile matter content of about 16 percent maintained a FSI of about 5.0 that is indicative of a good caking coal. This would indicate that the caking quality of a coal or char was not directly dependent upon the quantity of volatile matter it contained.

To get an insight into what was occurring to the volatile matter content and FSI of a coal during pretreatment, a series of tests was performed at different maximum temperatures. Each test of the series was performed with a 600-gram batch of Pittsburgh seam coal treated with steam plus 1 percent oxygen at atmospheric pressure at a gas velocity of 3 feet per second. Each batch was heated directly to 360° C in 25 minutes. After reaching 360° C, each individual batch of coal was heated to a designated temperature at 10° C intervals from 360° to 430° C. The coal was heated at a rate of 10° C per 25 minutes. Each test was concluded by rapid cooling with nitrogen as previously described.

Analysis of char taken at 10° C intervals during the gradual heating of a Pittsburgh seam coal through its plastic range indicates little change in the FSI from 360° to 400° C. Heating to 410°, 420°, and 430° C effected a rapid decline in the FSI of the coal-char to 4.5, 2.5, and 1.5, respectively. As shown in figure 8, the volatile matter content of the coal rapidly

decreased, following the same pattern as the FSI for every 10° C increase above 400° C. Each 10° C increase was accompanied by an increase in pretreatment time of 25 minutes; thus devolatilization was a function of both temperature and time.

The pretreatment technique developed offers promise, from an economic standpoint, as part of an integrated coal pretreatment and high pressure steam-oxygen-coal gasification process. The pretreatment can be performed at gasification pressure and part or all of the steam and a small part of the oxygen fed to the gasifier can be used as in the pretreatment. Furthermore, the gases and tars produced in pretreatment can be fed directly to the gasifier as fuel. Not only would this conserve energy, it would solve the effluent or off-gas problem from the pretreater. It is also conceivable that the pretreater vessels could serve as feed lock-hoppers for the pressure gasifiers, thus decreasing the net capital investment of the pretreatment.

#### CONCLUSIONS

A pilot plant study has shown that the caking property of a bituminous coal can be eliminated by pretreatment in a fixed bed. The caking quality of hvab, hvbb, and lvb coals was destroyed either by prolonged heating at the softening temperature followed by rapid heating through the plastic range with an inert gas containing a small amount of oxygen or by rapid initial heating followed by prolonged heating through the plastic range.

There was some variation in the conditions required for treating each coal, but generally hvab coals required about 180 minutes of pretreatment as compared to about 80 minutes for the hvbb coals. The chars produced did not cake when exposed to a hydrogen atmosphere at 500° C and 400 psig, indicating their suitability for use in fixed-bed gasification. The FSI served as a guide to indicate that the coal was no longer agglomerating. For most chars there was no agglomeration when the FSI declined to about 1.5 or lower.

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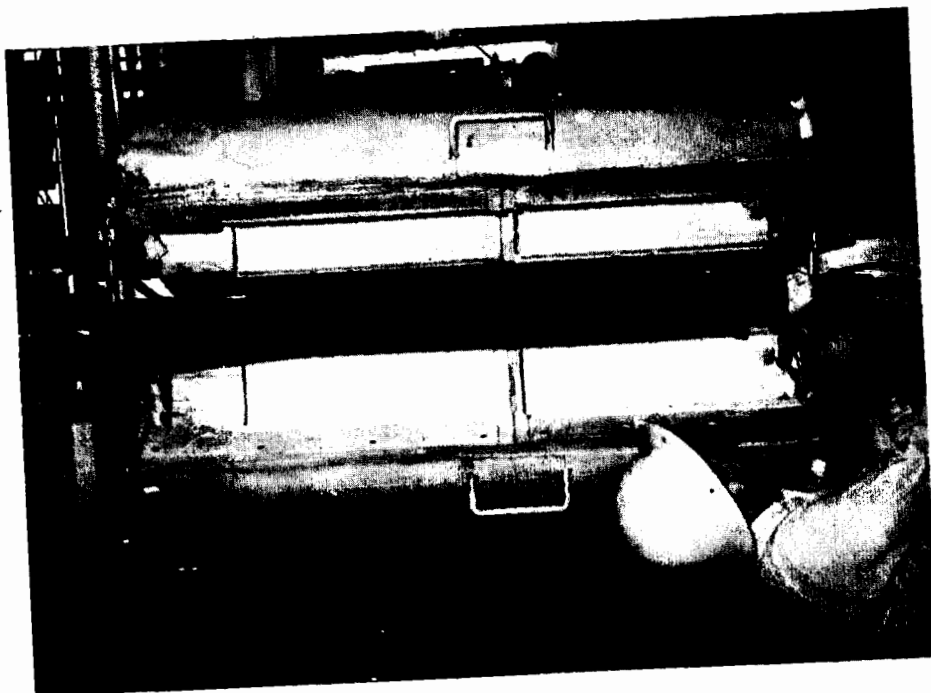


Figure 2

A View of the Vessel in Which the Coal is Pretreated.

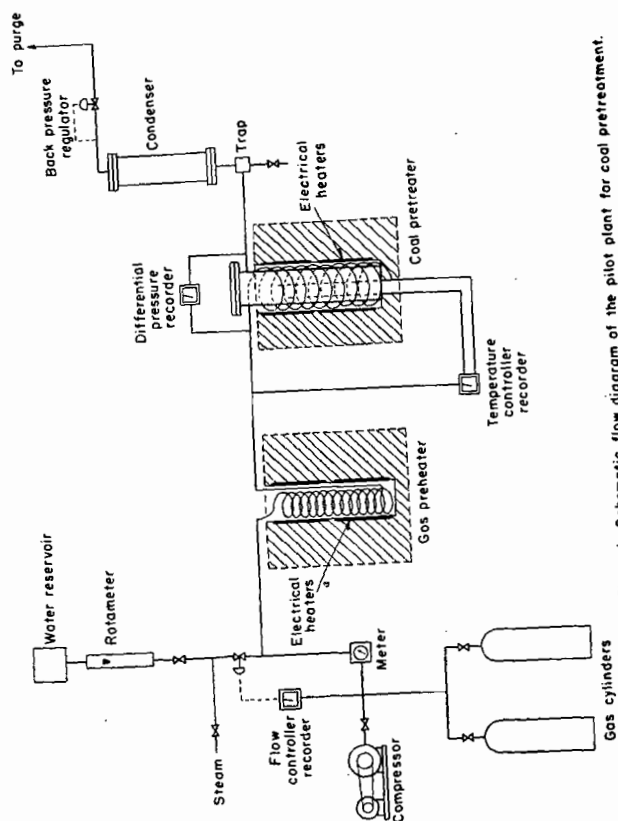


Figure 1.-Schematic flow diagram of the pilot plant for coal pretreatment.

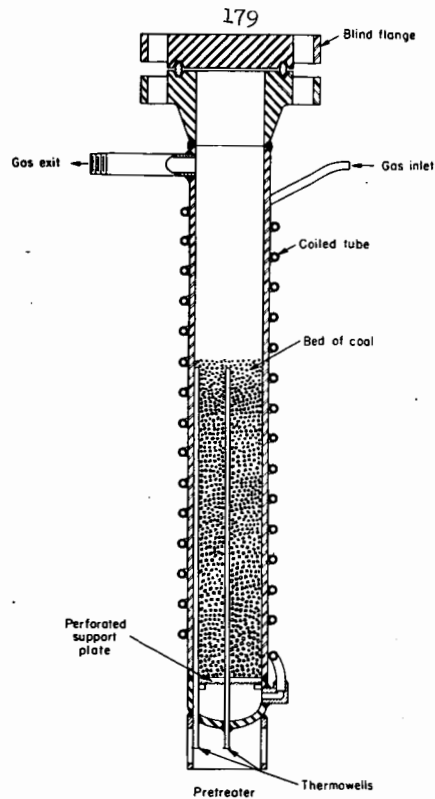


Figure 3—Cross-sectional view of the coal pretreater vessel.

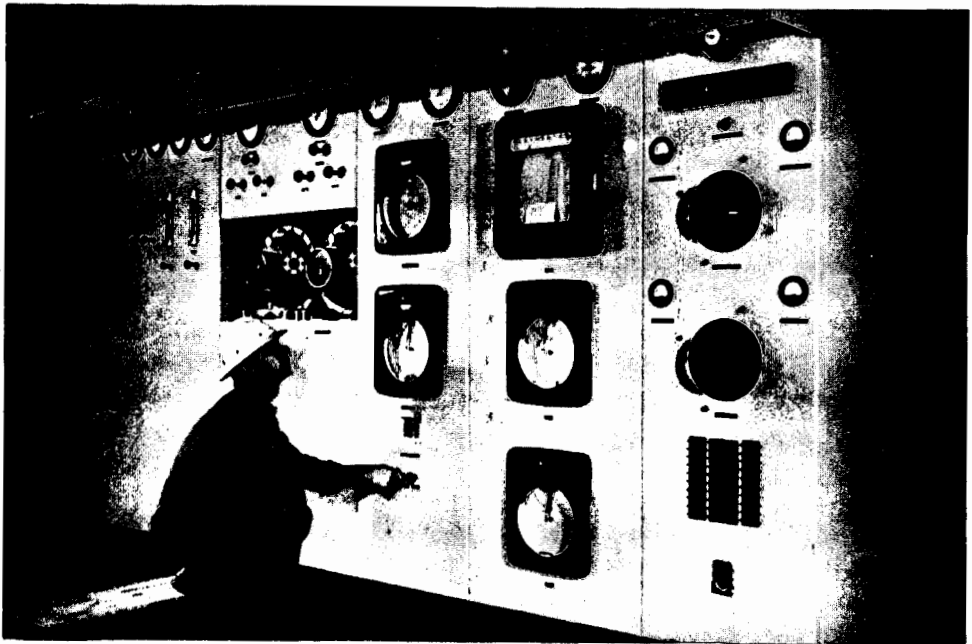


Figure 4. A view of the control panel for the coal pretreating pilot plant.

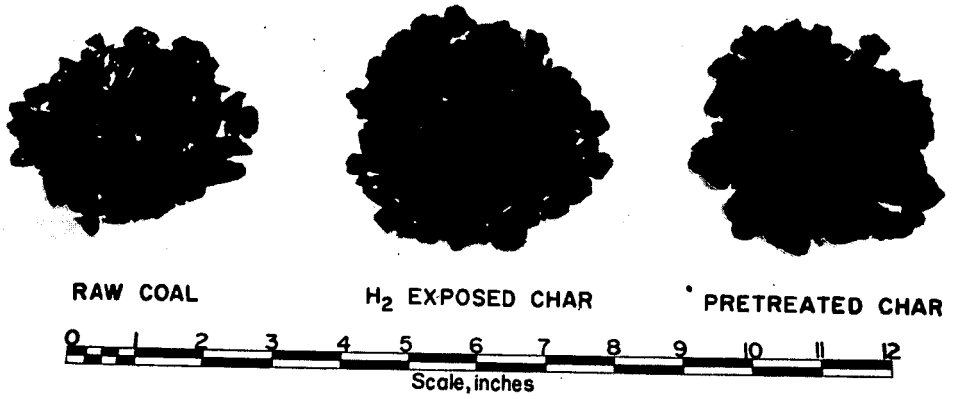


Figure 5. Raw coal used plus char from a typical pretreatment at 430 C and the same char exposed to hydrogen for 1 hour at 600 C and 400 psig.

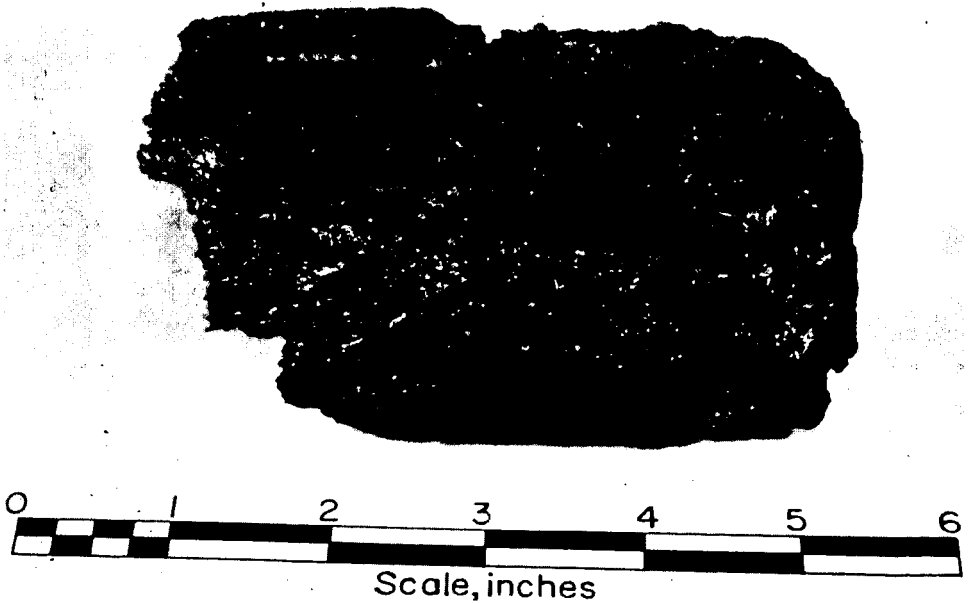


Figure 6.. Solid mass of char made from coal with no pretreatment.

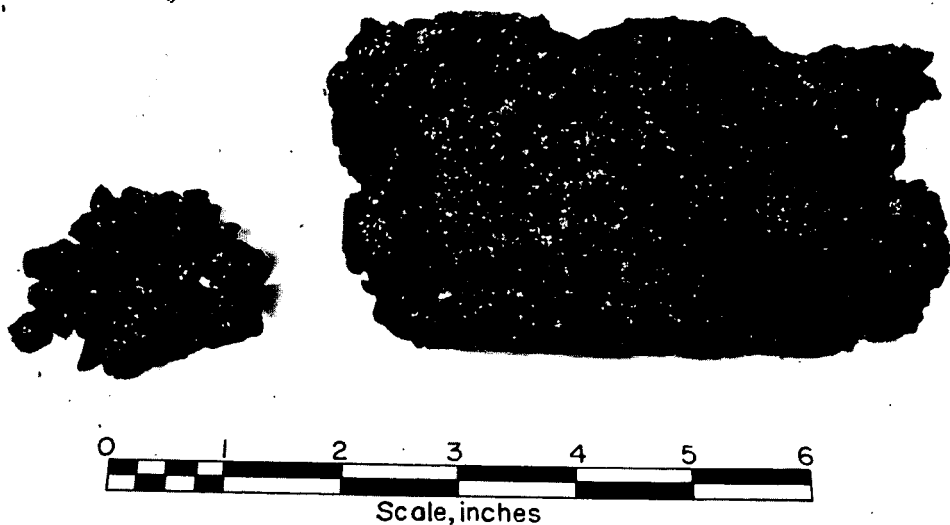


Figure 7. Mass of char containing discrete coal-char particles made from coal with some pretreatment.

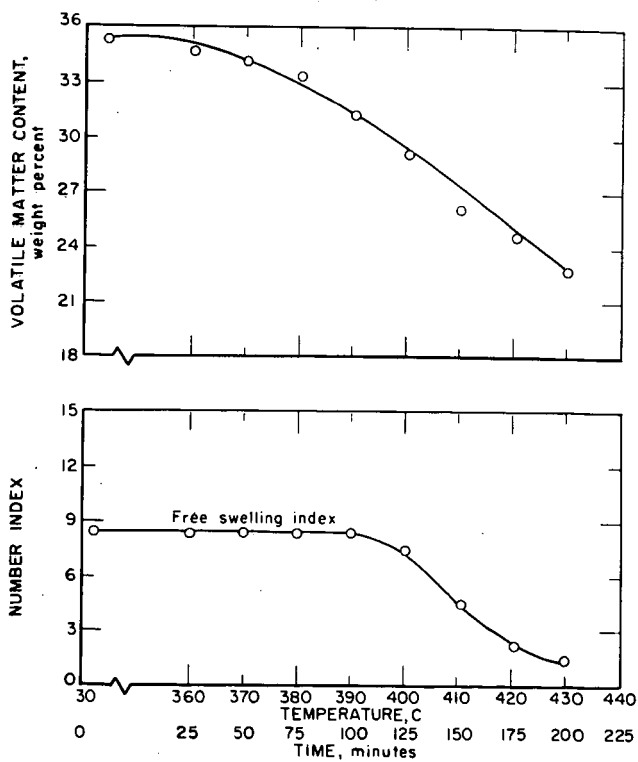


Figure 8.→Effect of temperature and pretreatment time on the free swelling index and volatile matter content of a Pittsburgh seam coal.

The Destruction of the Caking Properties of Coal  
By Pretreatment in a Fluidized Bed

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INTRODUCTION

Gasification of coal to make a synthesis gas that can be converted to fluid fuels is a means of supplementing the country's liquid and gaseous fuel supplies while at the same time increasing the market for coal. A large market for these fuels exists near the eastern coal-fields, but, unfortunately, eastern coals do not readily yield to gasification in commercial fixed-bed and fluidized-bed gasifiers. They become plastic and agglomerate when heated to the gasification temperature, the permeability of the bed to gas is reduced, and objectionable channeling occurs. The Bureau of Mines is investigating methods of pretreating coals to destroy their caking properties in order to overcome these obstacles to gasification. The ultimate objective is to develop a low cost process. The first phase of the work consisted of pretreatment studies in a fluidized bed using various fluidizing gases and operating conditions. The studies were conducted with strongly caking coals, typical of those in the East. The results of the study and the operating requirements necessary to destroy the caking properties of the selected coals are reported.

Other research has been done on methods to destroy the caking properties of these coals. Chanabasappa and Linden<sup>1</sup> pretreated coal to make a char for hydrogasification. They operated at 400° to 700° F using a steam feed of 4-5 standard cubic feet per pound bituminous coal. The time of treatment was 60-75 minutes. Nathan<sup>2</sup> patented a fluidized process for pretreating coal at a temperature of 316° to 441° C, requiring 10-60 minutes and using 0.02-0.08 pound of oxygen per pound coal feed. Char was recycled for temperature control. Karl<sup>3</sup> preheated bituminous coal to less than 400° C with a gas containing oxygen. Sylvander<sup>4</sup> also preheated coal, to a temperature below the plastic range, using oxygen. Welinsky<sup>5</sup> operated a fluidized carbonizer, the first stage at temperatures within the plastic range of the coal (725° to 825° F).

Recycle char from the second stage is added to the feed in the first. Foch<sup>9</sup> carbonized coal in a three-stage system. He dried and preheated coal to 570° to 750° F in the first stage using gases resulting from partial combustion of pyrolysis gases from the second stage. The preheated coal in the second stage is carbonized using preheated air. The char is cooled in the third stage.

When a caking coal is heated it becomes viscous and plastic at a given temperature range that is characteristic of the coal. This property makes caking coals nonusable in fluidized-bed and fixed-bed gasifiers because the coal sticks to the walls and the particles agglomerate. The Bureau investigated a combined thermal and mild oxidation treatment to destroy in a fluidized bed the caking properties of typical coals found in the eastern United States. Although the method described in this paper was successful it is not known definitely why the pretreatment makes the coal nonagglomerating. It cannot be attributed entirely to oxidation of the surface of the particles, because the resultant char contains less oxygen than the original coal. (See table 1.) Rapid thermosetting of the liquid phase as it forms may be an explanation, but this needs to be confirmed by experimental studies that are beyond the objectives of the investigation.

A variable study was made to determine operable conditions for pretreating the coal to a nonagglomerating state in the minimum time with the least loss of valuable components.

#### APPARATUS AND EXPERIMENTATION

A flowsheet of the bench-scale unit is shown in figure 1 and a photograph of the unit is shown in figure 2. The reactor is a 1-inch diameter stainless steel tube with an effective length of 18 inches. It is surrounded by electric heaters capable of heating the reactor to 900° C. Thermocouples are inserted both from the bottom and the top of the reactor. The usual method of operation is to heat the reactor while setting the proper gas velocity to give fluidization. This velocity was determined by experimentation in a glass tube at atmospheric temperature and pressure and then was corrected for the operational conditions. After the desired temperature is reached, the coal is charged to the reactor. The gases are collected after leaving the reactor and passing through a condenser and flask to remove the tars. When inert gas is used for treating the coal, the exit gas is not collected because the gas originating from the coal is too highly diluted by the inert gas to give significant results.

Different conditions of operation were tried in the development of the process. The following fluidizing gases were used:

Steam  
 Steam plus air  
 Inert gas ( $N_2 + CO_2 + 0.1-1.0$  percent  $O_2$ )  
 Nitrogen (contains 0.1-0.3 percent  $O_2$ )  
 Prepurified nitrogen (essentially  $O_2$ -free)  
 Helium (essentially  $O_2$ -free).

Heat was transferred to the coal through the reactor wall (gas entering cold) and from the preheated gas (reactor wall maintained at the same temperature as the bed).

Pittsburgh seam coal from the Bruceton mine was used principally, but Pocahontas, Illinois, Sewickley, and Taggart coals also were treated. The rank and analyses of the coals are shown in table 1. The free swelling indices of these coals range from 4.5 to 8.5. The free swelling index is indicative of the caking qualities of the coals. If the index is reduced below 2 by pretreatment, the residue is usually noncaking.

To supplement the indicated results from the free swelling index,<sup>7/A</sup> another test was devised to verify that the char was nonagglomerating. A sample of the char was placed in a ceramic boat and the boat placed in a quartz tube in an electric furnace. The char was heated to 600° C while pure hydrogen was passed through the tube. The char was considered noncaking if after hydrogen treatment it flowed freely out of the boat. Later, to test it more severely, the char was exposed to hydrogen at 900° C. Usually if the free swelling index was less than 2, the hydrogen test indicated noncaking also.

Because this pretreatment process was developed primarily to make a nonagglomerating fuel for a gasification process, the hydrogen test is more pertinent than the free swelling index test. As the char is fed into the gasification unit, it will come in contact with hot hydrogen-containing product gases of the gasifier, a condition simulated by the hydrogen test at 600° or 900° C.

#### DISCUSSION OF RESULTS

Initially Pittsburgh seam coal, 10-14 mesh, was used with inert gas or nitrogen as the treating gas. The gas velocity for fluidizing at atmospheric pressure was about 2.5 feet per second, and the expansion of the bed was about 100 percent. Early tests showed that the individual coal particles expanded 100 percent or greater at temperatures of 400° to 450° C. Because of the expansion of the treated particles and the fluidized bed, the size of the charge was limited to 35 grams (60 cc). When the fluidized bed of coal was heated indirectly by transfer through the reactor wall, the coal particles agglomerated and adhered to the wall, making the unit inoperable. However, when the heat was supplied by direct transfer from the

gas while the reactor wall was maintained at a temperature for adiabatic conditions, the coal's caking properties were destroyed by the treatment and the unit was operable. The coal particles swelled and became globular. Pretreatment was successful when inert gas, steam plus air, or nitrogen was used, whereas agglomeration occurred at the same operating conditions when helium, steam, or prepurified nitrogen was the treating gas. This difference in results was traced to the presence of a small quantity of oxygen (0.1-0.3 percent) in the inert gas and nitrogen, and the absence of a measurable quantity of oxygen in the other gases.

The effect of temperature on the caking properties of Pittsburgh seam coal is shown in figure 3. Four mesh sizes of coal were fluidized with an inert gas containing 0.8-1.0 percent oxygen. Plotted are the increase in volume, the weight loss of the coal, and the free swelling index of the resultant char with variation in treatment temperature. These results are more relative than absolute, but the trends of the different sizes are realistic. The larger particles were exposed to more oxygen than the smaller ones because the linear velocity was higher for the fluidization of the larger particles. The coal was maintained at the test temperature for 30 minutes in all tests. Poor fluidization occurred in all tests at 450° C, and with the 8-10 and 10-14 mesh sizes at 425° C. The 28-48 and 48-100 mesh were successfully pretreated at 425° C, as were all sizes at 400° C. While the fluidization of the coals was satisfactory in the reactor at 375° C, the chars caked when they were tested at 600° C with hydrogen, indicating insufficient treatment. The free swelling index test corroborates the hydrogen tests because the index was higher than 2 at 375° C and no higher than 2 for all tests at 400° C, and below 2 at 425° and 450° C. As the temperature of treatment increased, the weight loss increased as more of the volatiles were removed. There was a greater increase in bulk volume with increasing temperature. These tests showed that the caking quality of Pittsburgh seam coal of 28-48 and 48-100 mesh was destroyed at 400° to 425° C in 30 minutes.

The effect of pressure on the caking properties of Pittsburgh coal is shown in figure 4. During these tests a 48-100 mesh size coal was fluidized with an inert gas containing 0.8 to 1 percent oxygen for 30 minutes at 400° C. Chars made at all pressures were noncaking. The volumetric expansion became less as the pressure increased from 0 to 300 psig. The weight loss decreased as the pressure was increased from 0 to 75 psig, then did not change with further increase in pressure. A linear gas velocity of about 0.4 foot per second was necessary for fluidization of 48-100 mesh coal at all the pressures, so that at the higher pressures a larger quantity of gas flowed through the coal. Generally, there was no significant change due to pressure. The only novel effect occurred when the pressure was released when the char was removed from the reactor. Some of the particles seemed to explode, probably because trapped gas was released due to depressurization. This effect was observed at all pressures above atmospheric.



Varying the time of pretreatment of Pittsburgh seam coal of 18-100 mesh produced the results shown in figure 5. Nitrogen containing 0.2 percent oxygen was the treating gas, and operating temperatures were 400° and 425° C. As shown in this figure, the char made by treating at 425° C for five minutes could be subjected to a hydrogen atmosphere at 900° C without caking. The free swelling index of this char was 1.5. The weight loss of the coal was 10 percent. Pretreatment for only 1 minute at 425° C was enough to produce a char that did not agglomerate at 600° C with hydrogen. However, the free swelling index of the char was 6-1/2, still indicative of a caking coal. Apparently the test with hydrogen at 600° C is not severe enough to determine if the coal has been rendered noncaking throughout. Some difference between the free swelling index and hydrogen exposure tests can be expected because the char is ground for the free swelling index test but is used in its original state in the hydrogen tests. The weight loss in the 1-minute test was 8 percent. When the coal was treated at 400° C, the minimum pretreatment time was 20 minutes for the char to remain nonagglomerating in the hydrogen test at either 600° or 900° C. The free swelling index was 2, indicative of noncaking. The weight loss was 10 percent. Since the weight loss at both 400° and 425° C was about 10 percent, the higher temperature is more desirable because less time is required for treatment.

The effect of temperature on the volume and composition of the gas made during coal treatment with pure steam for 30 minutes at 375°, 400°, and 425° C is shown in figure 6. As the temperature increased, the hydrogen yield increased from about 5 to 9 cubic centimeters of gas per gram of coal charged. The methane yield increased from about 1 to 5 cubic centimeters per gram, and the C<sub>2</sub> yield increased also. The yields of carbon dioxide, nitrogen, carbon monoxide, and oxygen remained relatively constant. A gas of higher heating value was made at the higher temperature of operation.

The effect of varying the temperature of pretreatment of Pocahontas No. 4 (lvb), Taggart (hvab), Illinois No. 6 (hvbt), and Sewickley (hvab) coals is shown in figure 7. Nitrogen containing about 0.2 percent oxygen was used at a linear velocity of about 0.8 foot per second to fluidize the 28-48 mesh particles. Chars, made from Pocahontas or Illinois coal that had been treated at 375°, 400°, or 425° C, did not cake when subjected to a hydrogen test at 900° C. Taggart coal required treatment at 425° C to be satisfactory, while Sewickley could be treated at 400° only, as it agglomerated during pretreatment at 425° C and was ineffectively pretreated at 375° C. Taggart and Sewickley coals are similar in rank to Pittsburgh seam, all being hvab.

Pocahontas No. 4 and Illinois No. 6 require less drastic treatment than the hvab coals. This is not surprising for the lower rank Illinois coal, which has a free swelling index of 4.5 compared to 8-8.5 for the hvab coals. While the Pocahontas coal has the highest rank, it may respond to milder pretreatment because of its low volatile content. Taggart coal required treatment at 425° C. This coal also showed a drastic change in expansion as plotted in figure 7, having 0 percent volume increase at 375° C and 100 percent at 425° C.

These tests showed that the technique of pretreatment utilizing fluidization with gases containing small quantities of oxygen is applicable to several caking coals. However, conditions of pretreatment cannot be fixed exactly by the rank of coal; each coal must be tested to determine the most satisfactory temperature for pretreatment.

### CONCLUSIONS

The caking properties of coals tested could be destroyed by fluidizing the coal with a gas such as nitrogen, nitrogen plus carbon dioxide, or steam, containing at least 0.2 percent oxygen at 400° or 425° C. In a batch system, a thoroughly nonagglomerating char could be produced at 425° C in a 5-minute treatment using 18-100 mesh size coal. The caking property cannot be destroyed by the treatment described if oxygen is absent. It is desirable and may be necessary to heat the coal internally by the treating gas to prevent the particles from adhering to the wall of the reactor.

To obtain data that will permit a more exact evaluation of the process and estimate of the cost of this method of pretreatment, a study of a continuous system is needed. We plan to modify the bench-scale equipment for continuous feed of coal and removal of char. This will allow a realistic determination of the optimum feed gas-to-coal ratio and minimum average residence time required for pretreatment. In a fluidized bed all the coal is not pretreated for a uniform length of time because of the rapid mixing of the raw coal and treated char. The discharged solids will contain particles treated to different degrees because the residence time of the individual particles varies. The results of the batch study will be used as a guide for the continuous studies, but the optimum solids residence time and conditions of operation may be different from those obtained in the present investigation.

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- 7/ The treated or processed coal is designated as char in this report.

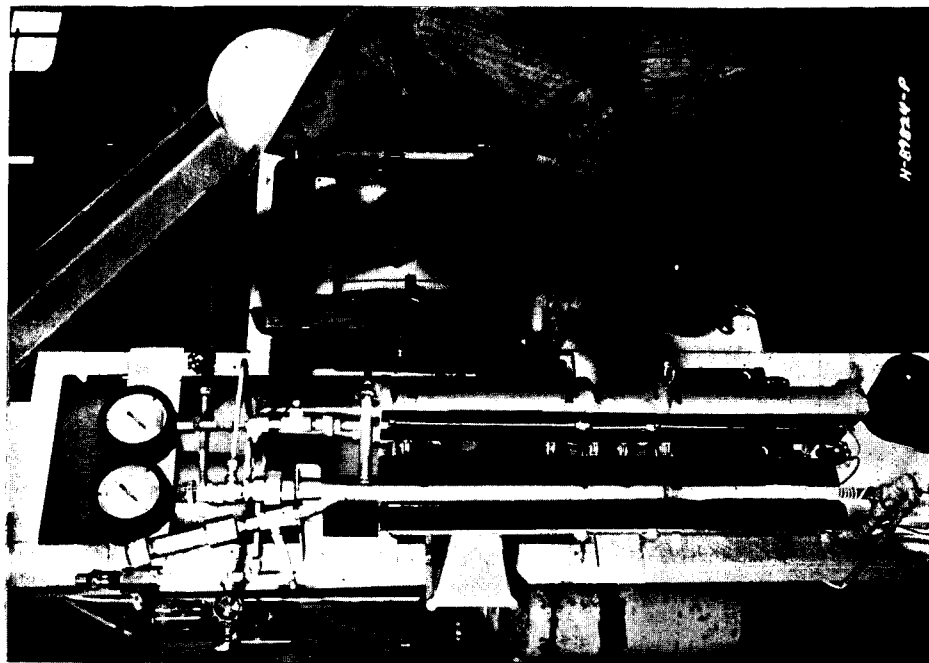
TABLE 1.- Analyses of coals and chars from pretreatment tests

Classification <sup>1/</sup>	Pocahontas #4		Taggart		Illinois #6		Sevickley		Pittsburgh	
	Raw	Char	Raw	Char	Raw	Char	Raw	Char	Raw	Char
<b>Proximate analysis, percent<sup>2/</sup></b>										
Moisture	2.7	0.4	1.1	0.1	6.1	0.5	1.3	0.4	1.7	0.8
Volatile matter	14.8	13.7	35.1	24.4	33.8	26.1	36.8	24.2	36.6	26.0
Fixed carbon	76.5	78.6	61.8	73.1	53.2	66.4	52.9	64.3	55.5	66.7
Ash	6.0	7.3	2.0	2.4	6.9	7.0	9.0	11.1	6.2	6.5
<b>Ultimate analysis, percent<sup>2/</sup></b>										
Hydrogen	4.4	4.0	5.4	4.7	5.2	4.4	5.2	4.4	5.3	4.6
Carbon	83.3	84.3	83.8	84.6	70.8	77.6	75.3	75.0	77.3	78.9
Nitrogen	1.3	1.3	1.5	1.6	1.7	1.9	1.6	1.7	1.6	1.7
Oxygen	4.5	2.6	6.6	6.0	14.3	8.1	6.5	5.2	8.4	7.2
Sulfur	0.5	0.5	0.7	0.7	1.1	1.0	2.4	2.6	1.2	1.1
Ash	6.0	7.3	2.0	2.4	6.9	7.0	9.0	11.1	6.2	6.5
Free swelling index	6.5	1.5	8	1.5	4.5	1.5	8.5	2	8.5	2
Heating value, Btu/lb	14,660	14,410	14,950	14,700	12,530	13,550	13,630	13,240	13,780	13,740

<sup>1/</sup> American Society for Testing Materials, Standard Specifications for Classification of Coals by Rank.

A.S.T.M. Designation D-388-38; A.S.A. M20.1-1938.

<sup>2/</sup> As received basis.



The Bench-Scale Unit for the Destruction of Caking Properties of Coal.

Figure 2.

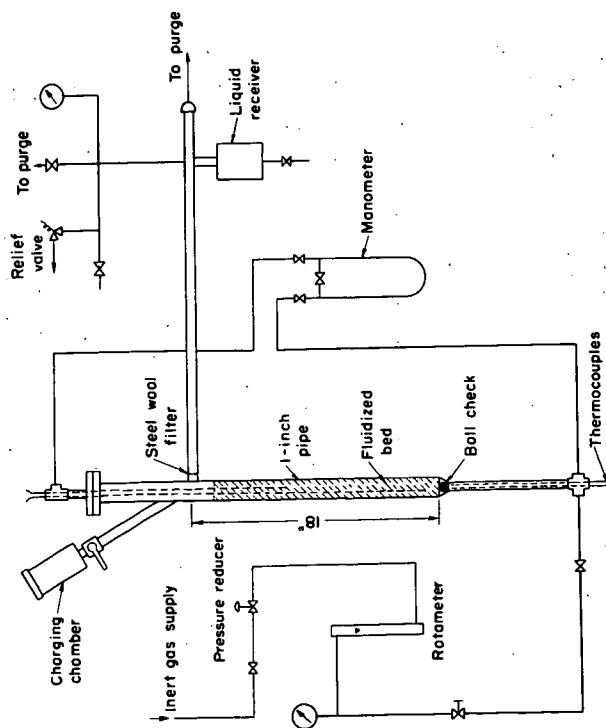


Figure 1.-1-inch reactor for pretreating coal in a fluidized bed. L-75

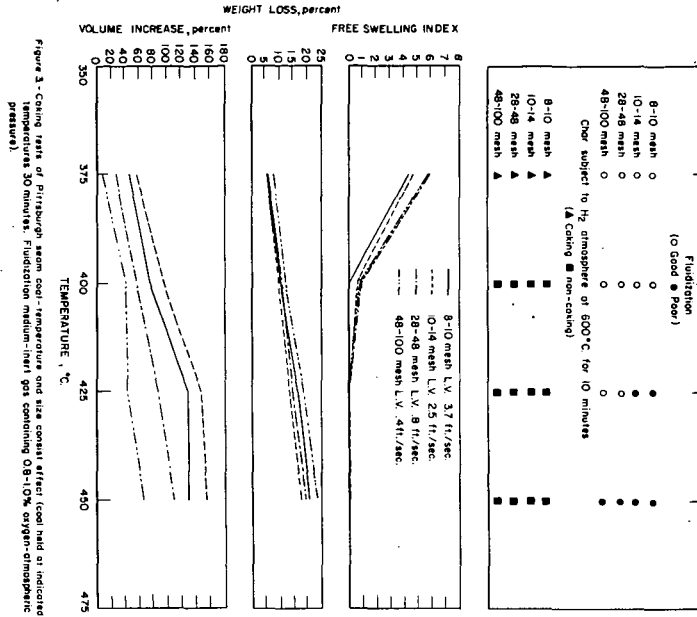


Figure 3.-Caking tests of Pittsburgh seam coal; temperature and size coast effect (coal held at indicated temperatures 30 minutes; fluidization medium-inert gas containing 0.8-1.0% oxygen-atmospheric pressure).

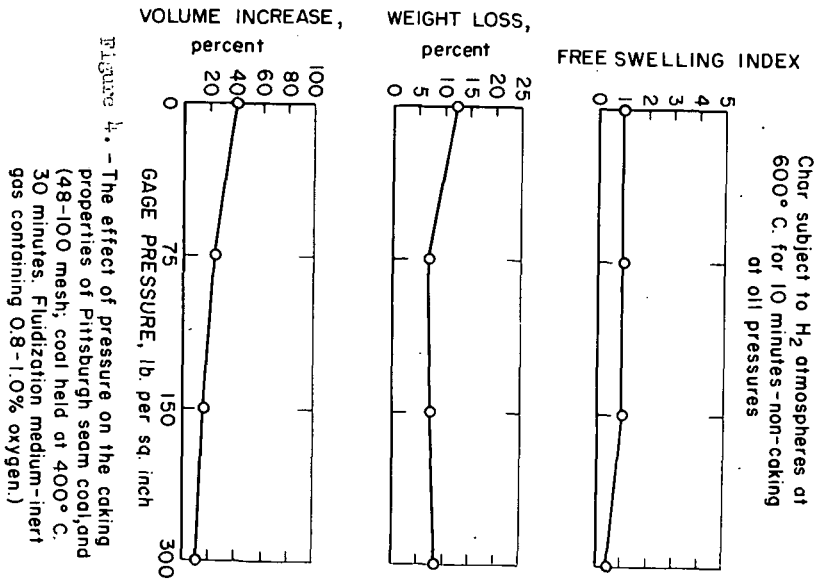


Figure 4.-The effect of pressure on the caking properties of Pittsburgh seam coal, and (48-100 mesh; coal held at 400°C, 30 minutes. Fluidization medium-inert gas containing 0.8-1.0% oxygen.)

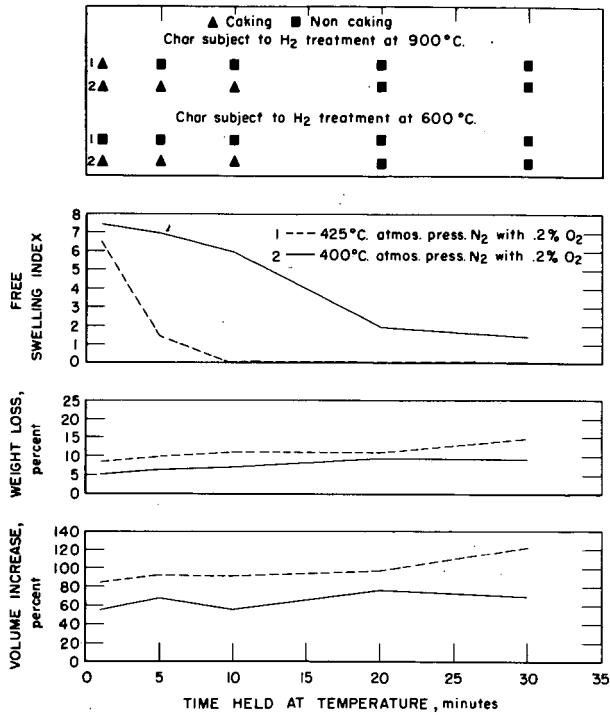


Figure 5.-The effect of time of pretreatment on the caking properties of Pittsburgh seam coal (18-100 mesh)

L-7891 1-17-63

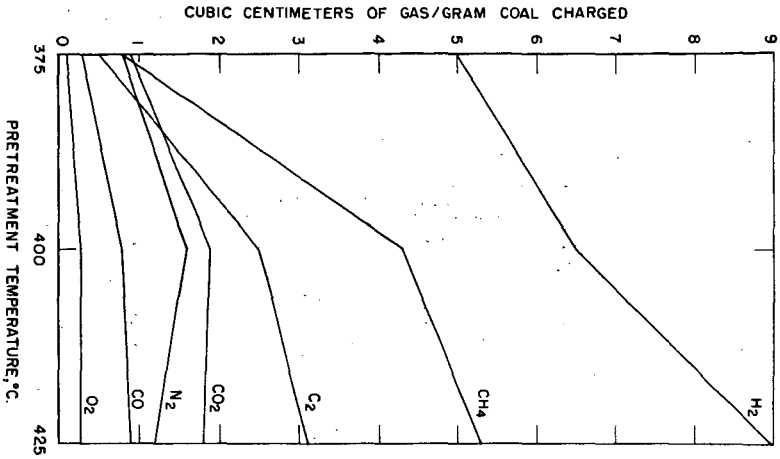


Figure 6.—The effect of temperature on the off gas made during steam pretreatment of Pittsburgh seam coal of 28–48 mesh. (Time of pretreatment 30 minutes).

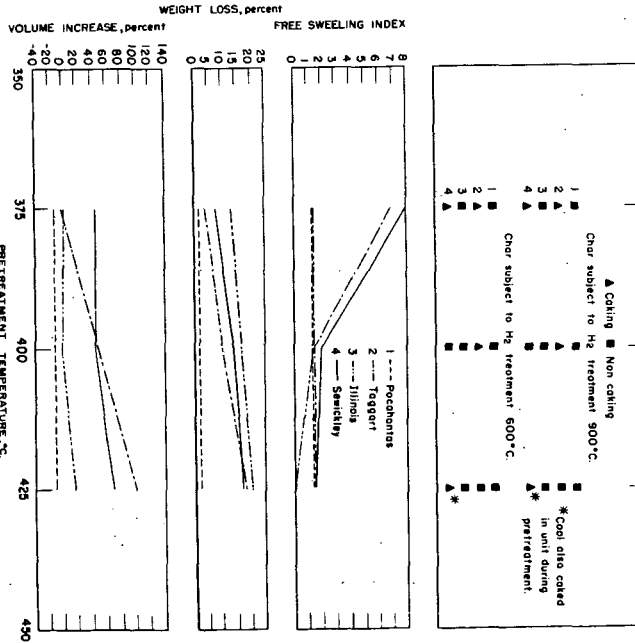


Figure 7.—The effect of temperature of pretreatment on caking properties of various coals 28–48 mesh. (Time of pretreatment 30 minutes).

**FLAMMABILITY CHARACTERISTICS OF METHYLACETYLENE,  
PROPADIENE AND PROPYLENE MIXTURES<sup>1/</sup>**

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**INTRODUCTION**

Methylacetylene and propadiene are used as welding and cutting fuels, as intermediates in chemical production, and as rocket fuels. Mixtures containing these combustibles in the gas phase are potentially hazardous because their vapors can decompose exothermally and propagate flame in the absence of oxygen. Heat from surroundings may be sufficient to effect their decomposition and ignition. With increasing temperature and pressure their thermal stability may be expected to decrease. The present investigation was conducted to determine the flammability characteristics of gas or liquefied gas mixtures containing these materials together with a hydrocarbon diluent, such as propylene or propane.

The fundamental properties of the methylacetylene decomposition flame at elevated pressures have been studied recently. Hall and Straker (1)<sup>2/</sup> report that its burning velocity is about 2 cm/sec between 10 and 40 atmospheres - a relatively low value in comparison to most known flames. They report a critical pressure for flame propagation of 43 psig (lower pressure limit) at about 20° C, in a 4-inch diameter tube. This may be compared with the critical pressure limit of 50 psig, in a 2-inch diameter tube, reported by Fitzgerald (2). Methylacetylene is more stable than acetylene which also forms a decomposition flame. The low pressure limit of acetylene in a 2-inch tube is only about 6 psig (3). Although little information is available on the stability of propadiene, recent experiments indicate that the energy requirements for the ignition of propadiene-methylacetylene mixtures are comparable to those required for the ignition of methylacetylene alone (4).

Like acetylene, methylacetylene and propadiene can be stabilized in a system at a specified temperature and pressure by adding inert gases or hydrocarbons that do not decompose under the given conditions. Fitzgerald (2) reports ethane to be a much better stabilizer than either methane or nitrogen. In the present study, the use of propylene and propane as diluents is examined because of the current interest in these hydrocarbons as stabilizers for methylacetylene and for methylacetylene-propadiene mixtures. The flammability characteristics of such mixtures (vapors) are shown to be sensitive to temperature and pressure, as well as to the size of the reaction chamber.

<sup>1/</sup> The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U. S. Department of the Interior and The Dow Chemical Company.

<sup>2/</sup> Numbers in parentheses indicate references at end of paper.



## EXPERIMENTAL APPARATUS AND PROCEDURE

Limit of Flammability Measurements

Flammability limits of the methylacetylene-propadiene-propylene system were determined at elevated temperatures and pressures in cylindrical stainless steel bombs measuring 1-, 2-, 4- and 12-inches in diameter, respectively, and in a spherical bomb of 24-inch diameter. The cylinders were about 42 inches long, except for the 12-inch diameter one which was 17 inches long. All of the bombs were insulated with asbestos and heated externally with Nichrome<sup>3/</sup> ribbon elements (see figure 1). Chromel-Alumel thermocouples (22-gage), located near the top and bottom of each bomb, were used to follow the heating of the test mixtures introduced into the vessels; thermocouple outputs were measured by a potentiometer. The partial pressure of each mixture component was measured by a mercury manometer or a Bourdon gage which also served to indicate if ignition occurred. A continuous pressure record was obtained during each experiment with an SIM Kistler transducer system whose output was fed to an oscilloscope equipped with a camera. In most determinations, the ignition source consisted of about 1 inch of 38-gage platinum wire located at the bottom of the test vessel.

In preparing for an experiment, a vapor mixture from the liquefied gases was made up in an explosion bomb which had previously been evacuated. To facilitate transfer of the gases from their supply cylinders, the latter were immersed in a water bath maintained at a selected temperature between 20° and 45° C; the explosion bomb was kept at the same temperature. Generally, at least one of the gases was introduced in two increments and alternately with the other gas or gases. To effect mixing, a thermal gradient of about 60 C° was maintained for at least one hour between the top and bottom of the bomb. Calculated mixture compositions, corrected for compressibility, were in close agreement with mass spectrometric analyses made for a few sample mixtures.

After the gases were mixed, the bomb was heated to the desired temperature and the platinum wire was fused. Ignition and extent of flame propagation was determined from the pressure measurements and from the amount of carbon formed. In some instances, complete analyses of the cooled product gases were made. Most of the experiments were performed at 120° C and at pressures of 50 and 100 psig.

The flammability of commercial mixtures (vapor) of liquefied gases was determined in much the same way. However, many of the flammability experiments were conducted at pressures greater than 100 psig and necessitated the transfer of appreciable quantities of the sample mixture to the bomb as a liquid. This was accomplished by first transferring a measured volume of liquid from the supply cylinder to an evacuated stainless steel sphere (523 cc); both were precooled with dry ice. The small sphere was then heated to force the liquid mixture into the bomb where the initial test pressure was controlled by varying the sample volume and bomb temperature. The subsequent procedure was similar to that in the previous experiments.

Two representative commercial mixtures were examined; their compositions are given in table 1. According to the manufacturer's analyses, mixture No. 1 contained about 41 volume-percent diluents, (mostly propane and propylene); mixture No. 2 contained about 32 volume-percent diluents (mostly propane). Mass spectrometric analyses of mixture No. 2 by the Bureau of Mines gave a diluent content of 43 volume-percent for the vapor sample and 29 volume-percent for the liquid sample. This variation can be attributed to the preferential distillation of the lighter diluent components.

<sup>3/</sup> Reference to specific brands, and make or models of equipment is made to facilitate understanding and does not imply indorsement of such items by the Bureau of Mines.

TABLE 1. - Composition of representative commercial mixtures of liquefied gases (volume-percent)<sup>1/</sup>

	Mixture No. 1	Mixture No. 2		
	Mfg.'s analysis (Liquid)	Mfg.'s analysis (Liquid)	BuMines analysis <sup>2/-</sup> (Liquid)	(Vapor)
Methylacetylene	36.1	27	(71	(57
Propadiene	23.3	41	(	(
Propane	22.5	28	22	37
Propylene	10.8	---	--	2
C <sub>4</sub> -Carbon cpds.	7.3	4	7	4

<sup>1/</sup> Supplied by The Dow Chemical Company.

<sup>2/</sup> Mass spectrometric analyses.

The methylacetylene used in this work had a minimum purity of 95 percent and could contain as much as 4 percent nitrogen according to the vendor's specifications; mass spectrometer analysis of our sample showed about 2 percent nitrogen present. The propadiene and propylene were about 97.5 and 99 percent pure, respectively; propylene was the main impurity in the propadiene.

## RESULTS AND DISCUSSION

### Flammability Limits of the Methylacetylene-Propadiene-Propylene System

Mixtures of methylacetylene and propadiene vapors were found to be flammable (in the absence of air) in all proportions at 120° C and 50 psig. Addition of propylene to either of these components produced limit mixture compositions which were dependent upon the temperature and pressure as well as on the vessel diameter. Limit compositions found at 120° C and at 50 or 100 psig are given in table 2 for vessel diameters of 1 to 24 inches. The data in table 2 were used to make up the ternary diagram shown in figure 2. This figure shows the approximate range of flammable mixtures for the methylacetylene-propadiene-propylene system under the experimental conditions noted. In any given vessel, the range of flammable mixture compositions is greatest with high concentrations of propadiene. For example, propadiene-propylene mixtures containing up to 31.3 percent propylene are flammable in the 12-inch diameter bomb at 100 psig; 21.9 percent is the limiting propylene concentration for methylacetylene-propylene mixtures.

The propadiene used in this investigation propagated flame at pressures in excess of 16 psig at 120° C in a 2-inch diameter bomb; the methylacetylene required pressures greater than 39 psig. Other investigators have reported similar pressure limits of 31 psig at 120° C and about 45 psig at 150° C for methylacetylene in 2-inch and 1-1/4-inch diameter bombs, respectively (2,4). It is not altogether surprising that methylacetylene should be more stable than propadiene, because the former contains a methyl group that provides increased resistance to thermal degradation. Pyrolysis experiments (400-650° C) by Meinert and Hurd (5) indicate the same order of stability for these liquefied gases. They also obtained evidence that methylacetylene first converts to propadiene, which then polymerizes and eventually decomposes.

TABLE 2. - Flammability limits of methylacetylene-propylene-propadiene mixtures at 120° C in various size vessels.<sup>1/</sup>

Initial Pressure psig	Methylacetylene Vol.-%	Propylene Vol.-%	Propadiene Vol.-%
<u>1-inch ID Bomb (0.47 liter)</u>			
100	92.8	7.2	--
100	--	19.8	80.2
<u>2-inch ID Bomb (2.03 liters)</u>			
50	94.7	5.3	--
50	--	15.3	84.7
100	90.4	9.6	--
100	--	23.8	76.2
100	39.4	21.5	39.1
<u>4-inch ID Bomb (7.86 liters)</u>			
100	84.5	15.5	--
100	--	28.7	71.3
<u>12-inch ID Bomb (31.0 liters)</u>			
100	78.1	21.9	--
100	--	31.3	68.7
<u>24-inch ID Bomb (118.7 liters)</u>			
100	>76	<24	--
100	--	32.5	67.5

<sup>1/</sup> Ignition source consisted of 1-inch of 38-gage platinum fuse wire.

The flammable range of the mixtures was noticeably greater at 100 psig than at 50 psig (figure 2). In view of the lower explosion pressure limits given above for methylacetylene and propadiene, it was to be expected that the flammability of the mixtures would be pressure-sensitive under the experimental conditions; even propylene will propagate flame at sufficiently high temperatures and pressures. It was also to be expected that an increase in temperature would widen the limits of flame propagation. In some preliminary experiments at 60° C and 50 psig, mixtures of methylacetylene and propylene failed to ignite in the 2-inch diameter bomb with the ignition source used (1 inch of 38-gage platinum wire); these mixtures ignited readily at 120° C and 50 psig in the same bomb. It is possible that with other ignition sources these mixtures would ignite and propagate flame at the lower temperature (60° C) since ignition energy requirements become most critical near the limiting pressure condition for flame propagation.

The effects of initial pressure, vessel diameter, and mixture composition were also reflected in the pressure measurements. Pressure-time records from experiments in the 1-, 2- and 4-inch diameter bombs with near-limit mixtures of propadiene-propylene and methylacetylene-propylene are shown in figure 3 (A and B); pertinent data from these records are given in table 3. The rates of pressure rise and the maximum explosion pressures developed decrease markedly with a decrease in bomb diameter. For example, the initial rates of pressure rise for the propadiene-propylene mixtures were 60 and 250 psi/sec in 1 and 4-inch diameter bombs, respectively; the

corresponding ratios of maximum explosion pressure to initial pressure were 2.15 and 5.82. Comparable data were obtained with methylacetylene-propylene mixtures. It was evident from these and other results that the heat losses were greatest for the smallest vessel. The quenching diameter for methylacetylene flames is reported to be less than 0.3 cm at 15 psia and 120° C (1); with propylene as diluent, the quenching diameter should be greater under the same conditions.

Explosion pressure-time histories for the flammability determinations conducted in the 2-inch diameter bomb with propadiene and methylacetylene at various initial pressures are also shown in figure 3 (C and D). Maximum explosion pressures were attained more rapidly with propadiene than with methylacetylene, at a given initial pressure. At the explosion pressure limit for propadiene (16 psig), the initial and maximum rates of pressure rise were only 25 and 55 psi/sec, respectively (table 3). These rates, and those obtained for mixtures of these gases with propylene, increased noticeably as the initial pressure and the diameter of the vessel were increased. Because of the relatively low rates of pressure rise observed in most of these determinations, the times required to reach a given pressure were long, as compared to those that are generally observed with combustible-oxidant mixtures in similar bombs. As noted in table 3, the times required to attain maximum pressures were greater than 1 second except in experiments conducted in the 4-inch diameter bomb; these data indicate the slow development and propagation of flame that can be expected in the decomposition of these materials.

The effect of vessel size on the flammability limits of methylacetylene-propylene mixtures at 120° C and 100 psig is illustrated in figure 4. The concentration of diluent (propylene) required to produce limit mixtures increased with an increase in vessel diameter from 1 to 12 inches; above 12 inches the diameter had little effect. The following equations were found to fit the experimental data by the method of least squares for the range of vessel diameters,  $d$ , indicated:

Methylacetylene-propylene mixtures:

$$\text{Vol.-% propylene} = 4.1 + 3.2 d - 0.14 d^2; \quad 1" \leq d \leq 12" \quad (1)$$

Propadiene-propylene mixtures:

$$\text{Vol.-% propylene} = 18.3 + 3.0 d - 0.16 d^2; \quad 1" \leq d \leq 12" \quad (2)$$

The volume percent of propylene is the amount required to obtain a limit mixture.

The vessel diameter effect observed for these mixtures can be attributed largely to the slow flame propagation obtained with these materials. During most of the burning period, the burning velocities probably did not exceed about 2 cm/sec, the value reported by Hall and Straker (1) for pure methylacetylene at 10 atmospheres. With such a low burning velocity, the total heat losses to the walls by conduction and radiation can be significant enough to cause flame extinction. It is to be expected that such effects would be most evident, as is the case here, for the smallest diameter vessels or those with the greatest contact area-to-volume ratio. Judging from the burning velocities and flame temperatures, heat losses due to radiation appear to be very important in the propagation of decomposition flames through methylacetylene and acetylene; observed flame temperatures are much less than values calculated assuming no radiation losses (6,7). However, it has not been established whether such heat losses alone determine the explosion pressure limits of these flames.

The main (cooled) decomposition products from methylacetylene and propadiene were found to be carbon, hydrogen and methane (table 4); small or trace quantities of ethane, ethylene and unreacted gas were also present. Similar results have been obtained with methylacetylene and with acetylene by other investigators (1,2).

TABLE 3. - Pressure data from flammability experiments with methylacetylene-propylene-propadiene mixtures at 120° C and at various pressures.

Propylene Vol.-%	Bomb Diameter inches	Initial Pressure, P <sub>1</sub> psig	Maximum Pressure, P <sub>2</sub> psig	Pressure Ratio, P <sub>2</sub> /P <sub>1</sub> psia/psia	Time to Max. Pressure <sup>1/</sup> sec	Initial Rate of Pressure Rise psi/sec	Maximum Rate of Pressure Rise psi/sec
<u>Methylacetylene</u>							
None	2	45	233	4.18	1.295	70	320
"	"	100	610	5.46	1.190	160	1060
<u>Propadiene</u>							
None	2	16.5	68	2.67	2.070	25	55
"	"	18.5	89	3.17	1.335	35	115
"	"	22	226	6.62	1.240	65	440
"	"	100	600	5.37	1.020	150	1180
<u>Methylacetylene + Propylene</u>							
6.9	1	82	173	1.95	2.020	50	60
5.0	2	50	289	4.71	1.330	90	470
7.9	2	90	458	4.53	1.310	115	630
15.0	4	100	690	6.24	0.790	270	1510
<u>Propadiene + Propylene</u>							
19.3	1	100	231	2.15	1.830	60	100
21.5	2	100	304 <sup>2/</sup>	2.79 <sup>2/</sup>	0.945 <sup>2/</sup>	160	430 <sup>2/</sup>
27.9	4	100	652	5.82	0.810	250	1490
20.2	2	100	419 <sup>2/</sup>	Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)	3.78 <sup>2/</sup>	145	810 <sup>2/</sup>
					1.195 <sup>2/</sup>		

<sup>1/</sup> Times measured from point of initial pressure rise.

<sup>2/</sup> Maximum pressures were not observed.

TABLE 4. - Decomposition products in flammability experiments with methylacetylene-propylene-propadiene mixtures at 120° C and at various pressures

Initial Propylene Content, Vol.-%	Bomb Diam- eter, inches	Initial Pres- sure, psig	Carbon Formed, gms	Gaseous Products (Vol.-%)							Carbon Conver- sion, %	
				Hydro- gen	Methane	Ethane	Ethyl- ene	Nitrogen & Carbon Monoxide	Unre- acted Gas	Hydrogen - Carbon Mole Ratio Input      Output		
None	2	42	6.61	71.0	25.4	0.3	0.2	1.8	1.3	1.33	1.44	71
"	"	45	6.92	--	--	--	--	--	--	--	--	71
"	"	60	9.19	--	--	--	--	--	--	--	--	74
"	"	100	13.89	73.4	19.0	0.1	0.1	1.8	5.6	1.33	1.48	73
None	2	16.5	2.89	61.5	29.8	Propadiene 0.6      2.3		0.7 <sup>2/</sup>	5.1	1.33	1.36	58
"	"	18.5	3.48	--	--	--	--	--	--	--	--	67
"	"	50	7.65	72.7	20.9	0.3	0.3	2.3	3.5	1.33	1.40	74
"	"	100	15.69	81.7	16.3	0.1	0.1	--	1.8	1.33	1.42	82
<u>Methylacetylene + Propylene</u>												
6.9	1	82	1.52	--	--	--	--	--	--	--	--	40
7.9	2	90	12.28	--	--	--	--	--	--	--	--	70
15.0	4	100	60.68	79.1	18.2	--	--	1.7	1.0	1.43	1.75	82
<u>Propadiene + Propylene</u>												
19.3	1	100	1.80	--	--	--	--	--	--	--	--	42
23.3	2	"	13.90	--	--	--	--	--	--	--	--	75
27.9	4	"	56.81	--	--	--	--	--	--	--	--	80
<u>Methylacetylene (50%) + Propadiene (50%)</u>												
None	2	50	7.58	--	--	--	--	--	--	--	--	74
<u>Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)</u>												
20.2	2	100	13.55	--	--	--	--	--	--	--	--	74

1/ Mole percent of available carbon converted to free carbon.  
2/ Benzene.

<sup>1/</sup> Mole percent of available carbon converted to free carbon.  
<sup>2/</sup> Benzene.

However, acetylene generally undergoes more complete decomposition to the elements, (carbon and hydrogen) at the temperatures and pressures employed here. Hydrogen production increased with an increase in initial pressure whereas the methane content decreased. Ethane and ethylene were barely detectable in the products formed at the maximum pressure (100 psig), but they were present in significant amounts (0.6 percent ethane and 2.3 percent ethylene) in the experiment with propadiene at a pressure of 16.5 psig; benzene (0.7 percent) was also found at this low pressure. The same gases form as products of the explosive decomposition of ethylene at elevated temperatures and pressures (8). Hurd and Meinert also report similar products from the pyrolysis of propylene between 600° and 955° C (9); however, they did not find any evidence of aromatic hydrocarbons in the pyrolysis of methylacetylene or propadiene between 400° and 650° C (5).

Figure 5 shows that the amount of free carbon formed was nearly insensitive to mixture composition and increased linearly with initial pressure; these data were obtained at 120° C in the 2-inch diameter bomb. The experimental carbon yield is compared to that which would be expected from the assumed reactions that identify the three curves given in this figure. It is seen that the experimental data fall essentially between the bottom and middle curves which correspond to carbon yields of 2 and 2-1/2 moles, respectively, per mole of methylacetylene ( $\text{HC} \equiv \text{C}-\text{CH}_3$ ) or propadiene ( $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ ). However, the gas compositions of the cooled combustion products were not altogether consistent with those of the reactions assumed here.

Material balances based on the complete analyses of the combustion products from methylacetylene and propadiene are given in table 5. As the decomposition products were largely carbon, hydrogen and methane, small quantities of ethane, ethylene, etc. were neglected. Best material balances were obtained in the experiments at 100 psig.

TABLE 5. - Products formed by the explosive decomposition of methylacetylene, propadiene, and methylacetylene-propylene mixtures at 120° C and various initial pressures

Initial Pressure psig	Bomb Diameter inches	Reactants (moles) <sup>1/</sup>	Carbon moles	Hydrogen moles	Methane moles
42	2	(1) $\text{HC} \equiv \text{C}-\text{CH}_3$	2.16	1.08	0.39
100	"	"	2.34	1.34	0.35
16.5	"	(1) $\text{H}_2\text{C}=\text{C}=\text{CH}_2$	1.86	0.75	0.36
50	"	"	2.36	1.19	0.34
100	"	"	2.54	1.44	0.29
100	4	(1) $\text{HC} \equiv \text{C}-\text{CH}_3$ + (0.175) $\text{H}_2\text{C}=\text{CH}-\text{CH}_3$	2.96	2.00	0.46

<sup>1/</sup> Numbers in parentheses indicate moles of reactant.

essentially, only small amounts of additional carbon are needed to obtain agreement between the input and output materials at this pressure. The mole ratio of total hydrogen to carbon was 1.33 for both reactants; it was between 1.36 and 1.48 for their reaction products, including minor constituents such as ethane, ethylene, etc. (table 4). The apparent shortage of carbon may be ascribed to the fact that all of the carbon formed in the reaction vessel was not removed and weighed. The amount of hydrogen and other gaseous products combined or adsorbed in the carbon probably did not introduce a serious error.

The combustion products from an ignition in the 4-inch diameter bomb with 85 percent methylacetylene and 15 percent propylene at 100 psig and 120° C were also analyzed (table 4). The products were again chiefly carbon, hydrogen and methane, and the material balance was much like that observed with methylacetylene or propadiene alone (table 5).

The relative concentrations of hydrogen and methane that were found in the decomposition products may be explained partly by consideration of the decomposition of methane as follows:



According to thermodynamic data, little methane should exist at about 1500° C (10); therefore, maximum conversion of methane to carbon and hydrogen should occur at temperatures equal to or greater than this value. Since the observed flame temperatures for the decomposition of methylacetylene are about 1300° C (6), noticeable methane concentrations should then be expected in the end products. With decreasing pressure and vessel size, the heat losses increase and the ratio of methane to hydrogen should increase, as it actually did. In comparison, the decomposition of acetylene is associated with higher flame temperatures which account in part for the small amount of methane that is generally found in the decomposition of this material.

#### Flammability Characteristics of Representative Commercial Mixtures of Liquefied Gases

Vapors of commercial mixture No. 1 (41% diluents) did not propagate flame without air in the 2-inch diameter explosion bomb at temperatures extending from 18° to 187° C and at corresponding pressures of 80 to 390 psig; the only evidence of reaction was the presence of small quantities of liquid products and of carbonaceous soot near the ignition element. In most of these experiments, the ignition element consisted of two platinum wires (38-gage and 1-inch long) and 50 mg of guncotton.

Commercial mixture No. 2 (32% diluents) showed little evidence of reaction in flammability tests conducted in the 24-inch spherical bomb at 126° C and pressures up to 116 psig. However, at about 215° C and 285 psig, the mixture decomposed explosively in the 4-inch diameter cylindrical bomb, and the maximum pressure developed was greater than 1000 psig. Ignition occurred without fusion of the ignition source indicating that the mixture temperature (215° C) was sufficient to ignite the guncotton; spontaneous ignition of the mixture was unlikely in the absence of air at the above temperature and pressure.

According to the data obtained for various mixtures of methylacetylene, propadiene and propylene, commercial mixture No. 1 should not be flammable under the experimental conditions used here because of its high diluent content (22.5% propane, 10.8% propylene, and 7.3% 4-carbon atom hydrocarbons). Figure 2 shows that this mixture composition does not fall in the flammable range, assuming that the diluents are as stable as propylene. However, a moderate increase of the methylacetylene or propadiene concentration would tend to make the mixture flammable. Moreover, the mixtures will tend to be more unstable at higher temperatures and pressures. As the composition of commercial mixture No. 2 falls close to the range of flammable methylacetylene-propadiene-propylene mixtures (figure 2), its behavior at high temperatures and pressures is not surprising.



The ability of paraffin hydrocarbon diluents to stabilize liquefied gases appears to depend partly upon the heat of formation of the diluent. For example, the stability of methylacetylene (2) and acetylene (3) increases with the addition of paraffins of increased molecular weight and decreased heat of formation (negative). The effectiveness of these diluents and of nitrogen decreases in the following order:

Butane > propane > ethane > methane > nitrogen .

Thus, butane and propane should be preferred as stabilizers for these commercial mixtures; they should also be favored over propylene which has a positive heat of formation. The ability of the diluents to absorb heat can also be an important factor here and probably accounts to a large extent for the greater effectiveness observed with hydrocarbons than with nitrogen.

### CONCLUSIONS

Mixtures of methylacetylene and propadiene vapors are flammable in all proportions at an initial temperature of 120° C and a pressure of 50 psig. Nonflammable mixtures are formed by adding propylene and are dependent on such variables as temperature, pressure, vessel diameter, and ignition energy. The range of flammable mixtures increases when the initial pressure is increased from 50 to 100 psig. It increases also when the diameter of the reaction vessel is increased from 1 to 12 inches; above 12 inches the diameter has little effect.

The low pressure (explosion) limits are about 16 psig for propadiene, and 39 psig for methylacetylene at 120° C in a 2-inch diameter bomb. Initial rates of pressure rise following ignition of the test materials are very low and are indicative of unusually low burning velocities. These rates increase with an increase in vessel diameter and pressure.

The end products formed by explosive decomposition of methylacetylene between 42 and 100 psig and of propadiene between 16 and 100 psig are chiefly carbon, hydrogen and methane; methylacetylene-propylene mixtures give similar products. An increase in pressure increases the percentage of hydrogen and decreases the percentage of methane. Decomposition of these liquefied gases to their elements was less complete than that of acetylene at the same conditions.

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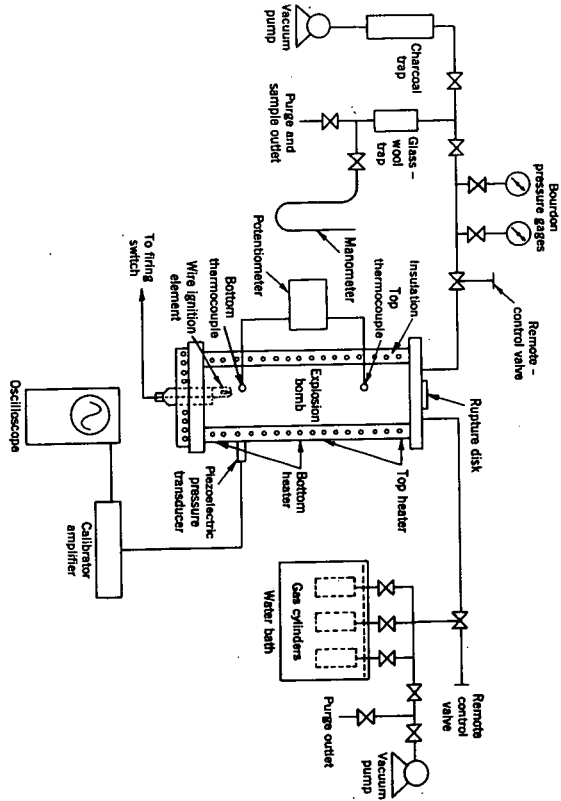


Figure 1. - Experimental setup for flammability determinations.

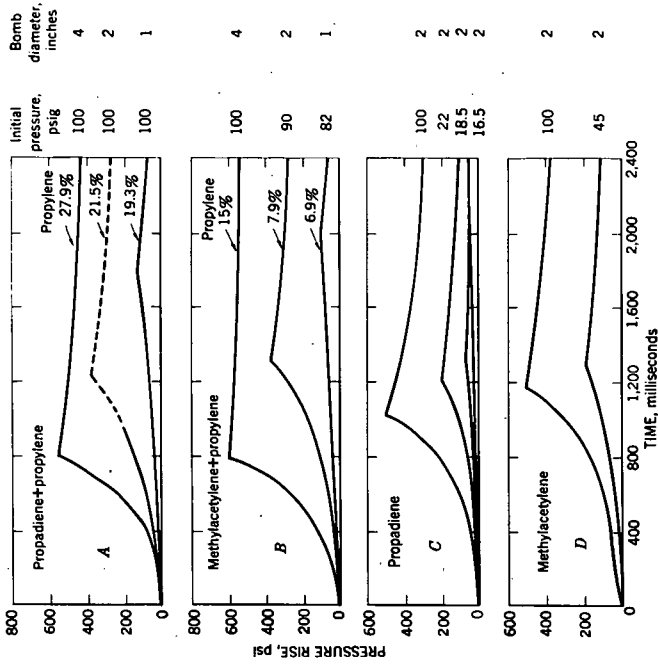


Figure 3. - Pressure-time records following the ignition of methylacetylene, propadiene and propylene mixtures at 120° C and various initial pressures.

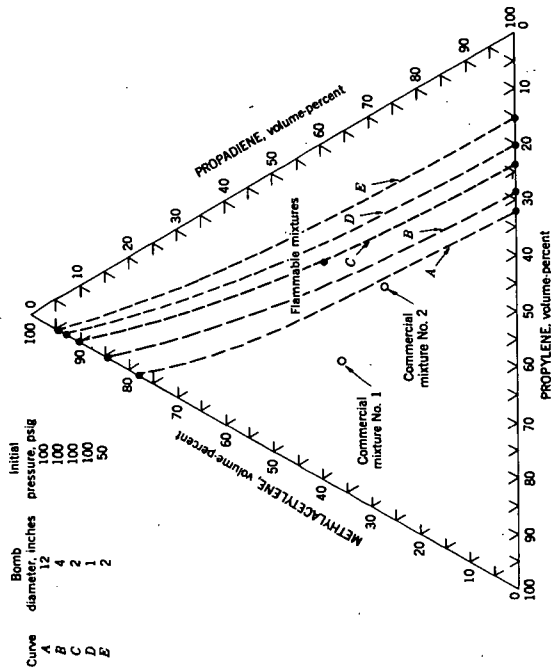


Figure 2. - Range of flammable mixtures for the methylacetylene-propadiene-propylene system at 120° C and at 50 and 100 psig.

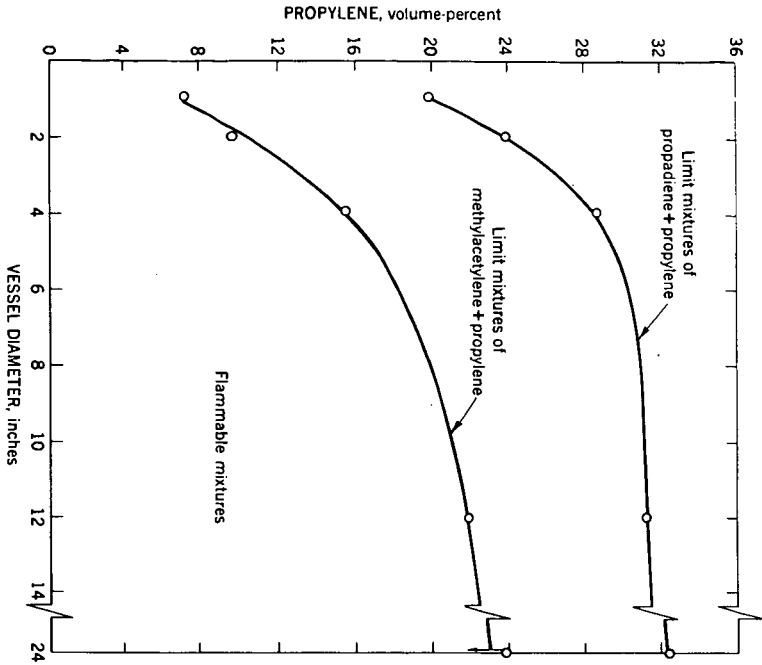


Figure 4. - Effect of vessel diameter on limits of flammability of methylacetylene-propylene and propadiene-propylene mixtures at 120° C and 100 psig.

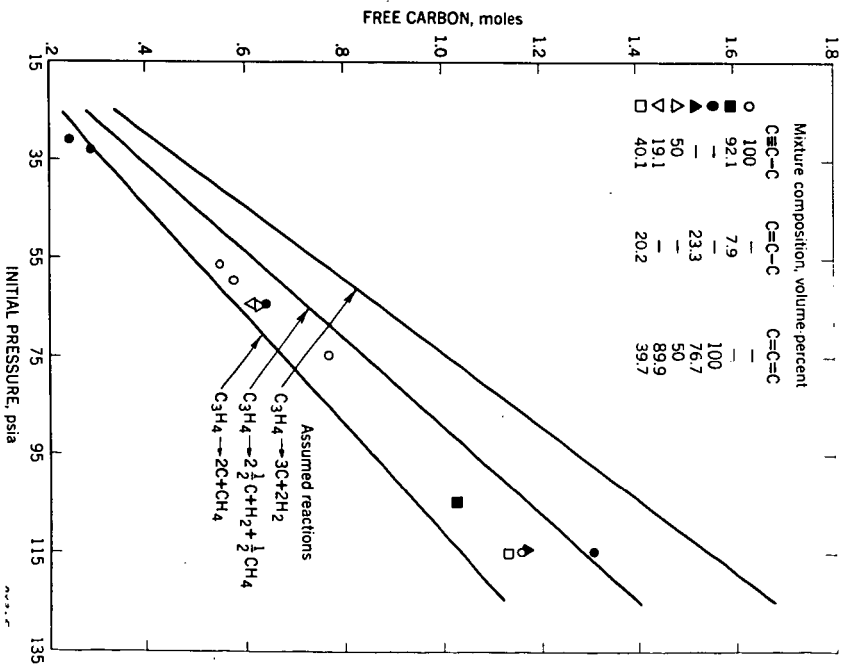


Figure 5. - Free carbon formed in explosive decomposition of methylacetylene, propadiene and propylene mixtures at 120° C and various initial pressures (2-135 psi diameter bomb).